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May 1987

AN EVALUATION OF PRISTINE LIGNIN FOR HAZARDOUS WASTE TREATMENT

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A feasibility study was conducted to assess the utilization of lignin, isolated from a steam-exploded hardwood (Tulip poplar) with 95% ethanol and 0.1n NaOH, as a potential adsorbent for hazardous waste treatment. Eight organic compounds and two heavy metals were selected to allow comparison of lignin isolates with activated carbon.

Adsorption kinetic studies, adsorption size studies, and adsorption isotherms based on the Freundlich equation were completed. The lignin isolates were extensively characterized using instrumental and classical wet techniques.

It was found that the adsorption capacity of lignin for heavy metals (chromium and lead) is comparable to activated carbon, despite a hugh divergence in surface area (0.1 m^2/g vs. 1000 m^2/g). The surface area discrepancy and the extensive aromatic substitution in lignin macromolecule impeded the achievement of an adsorption capacity of lignin for polar organic compounds which would allow it to be cost-competitive with activated carbon although results with phenol and, to a lesser degree, naphthalene indicate significant potential for achieving competitive capacities. A recommended plan for surface area and structural enhancement is is presented on the basis that lignin can be developed as an effective and low-cost adsorbent for polar priority pollutants and/or as an ion-exchange resins for heavy metal wastewater clean-up.

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ABSTRACT

A feasibility study was conducted to assess the utilization of lignin, isolated from a steam-exploded hardwood (Tulip poplar) with 95% ethanol and 0.1N NaOH, as a potential adsorbent for hazardous waste treatment. Eight organic compounds and two heavy metals ions were selected from the USEPA priority pollutant list for use as model compounds and to allow comparison of lignin isolates with activated carbon.

Adsorption kinetic studies, adsorption size studies, and adsorption isotherms based on the Freundlich equation were completed. The lignin isolates were extensively characterized using instrumental and classical wet techniques. Carbon adsorption isotherms were produced for compounds not reported in the literature.

It was found that the adsorption capacity of lignin for heavy metals (chromium and lead) is comparable to activated carbon, despite a huge divergence in surface area (0.1 m^2/g vs. 1000 m^2/g). The surface area discrepancy and the extensive aromatic substitution in lignin macromolecules impeded the achievement of an adsorption capacity of lignin for polar organic compounds which would allow it to be cost-competitive with activated carbon although results with phenol and, to a lesser degree, naphthalene indicate significant potential for achieving competitive capacities. A recommended plan for surface area and structural enhancement is presented on the basis that lignin can be developed as an effective and low-cost adsorbent for polar priority pollutants and/or as an ion-exchange resin for heavy metal wastewater clean-up.

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SECTION 1.

INTRODUCTION

PROBLEM, APPROACH, AND BENEFITS

The Handbook of Hazardous Waste Management (1) cites 26 operations for the cleanup of hazardous waste streams (Table 1). Some of these processes or operations are distinguished from others by the nature of active material which is central to the process, e.g., carbon adsorption is a special case of general adsorption. In a similar manner, an additional, and innovative, process for the capture and concentration of hazardous waste compounds such as heavy metals, organic acids, ketones, etc. which are found in aqueous waste streams has been proposed. The process involves the use of "pristine lignin" which Georgia Tech investigators had demonstrated as being readily isolated from woody wastes and raw materials by hydrothermal treatment and solvent extraction (2a-g). The production process for the lignin appeared to be economically feasible and all requisite process equipment for production of the lignin was commercially available. Unlike "commercial lignins", the "pristine lignin" is a clean, tractable, relatively low-molecular weight polymer with an expected high degree of organic functionality, unadultered by adventitious impurities. As such it was considered that the pristine lignin could be employed in one of three general ways, with or without chemical modification, viz.,

1. Adsorption
2. Ion-exchange chromatography and electron-exchange chromatography
3. Precipitation/Coagulation/Flocculation

Table 1 Treatment Processes

Carbon Adsorption
Centrifugation
Dialysis
Dissolution
Distillation
Electrodialysis
Electrophoresis
Evaporation
Filtration
Flocculation
Flotation
Freeze Crystallization
Liquid Ion Exchange
Liquid-Liquid Extraction of Organics
Microwave Discharge
Neutralization and pH Content
Precipitation
Resin Adsorption
Reverse Osmosis
Sedimentation
Steam Distillation
Steam Stripping
Ultrafiltration
Zone Refining

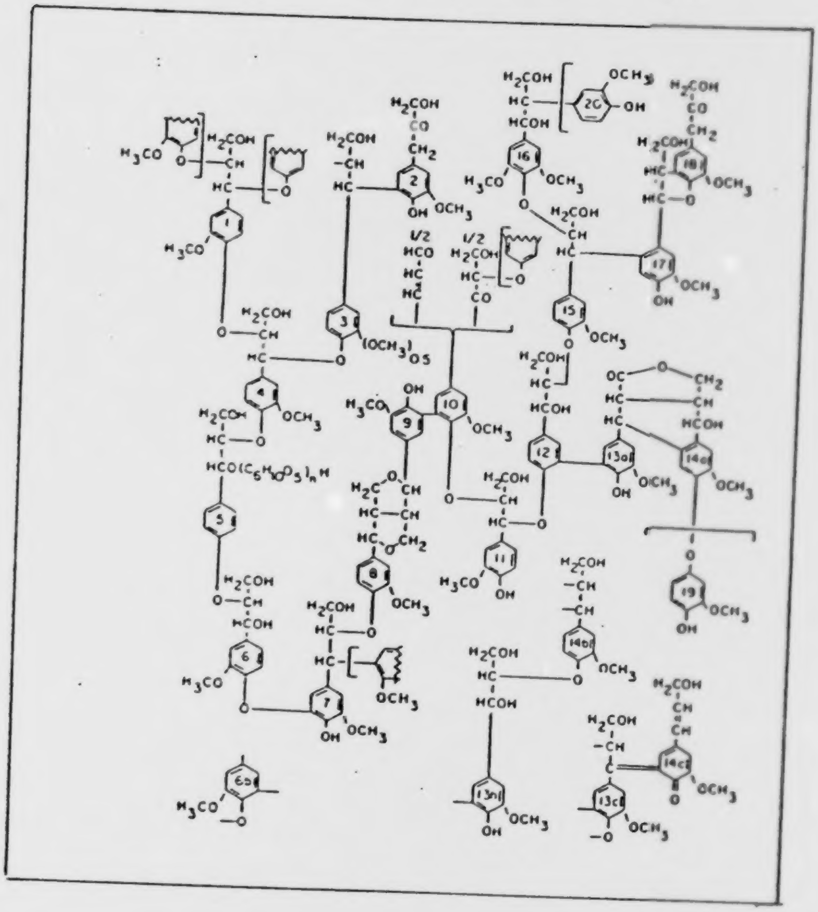
Air Stripping
Calcination
Suspension Freezing
Freeze-Drying
High Gradient Magnetic Separation
Ion Exchange

Because of this flexibility in unit operations options, and the need for research and development, it was premature to specify a preferred treatment process configuration. The principal economic merit of the proposed treatment with pristine lignin was forecast to be its low cost, particularly when compared to adsorbents such as activated carbon and commercial ion-exchange resins. To illustrate the economic advantage, a preliminary design and cost estimate was expressed.

It was believed that the use of "pristine lignin" would be exceptionally attractive for several reasons:

1. Low cost.
2. Readily disposable after use by incineration or pyrolysis/ gasification.
3. Metals readily reclaimable after treatment with lignin.
4. Biologically resistant.
5. High resistance to degradation/deploymerization.
6. Naturally abundant in nature; coniferous woods (28%), rice hulls (40%), barley straw (16-22%), bagasse (20%).
7. High rich organic functionality, e.g., phenolic hydroxyl groups on the aromatic nuclei. Also, quinonic groups, carboylic acids, carbonyl moieties, etc. (See Figure 1).
8. Cation complexation, i.e., heavy metal trapping.
9. Organic complexation, e.g., simple phenols, etc.
10. Oxidation-reduction exchange potential due to quinone and diphenoquinone groups possible, i.e., reduced ionic mobility.
11. No need for radical engineering redesign with this technology.
12. Relatively well-established science and technology base for lignin modification.

Fig. 1 Lignin (sans Quinone Groups)



13. Modified versions can range from aqueous solubility (pH-controlled) to organic soluble.
14. Existing, though small, commercial markets for crude lignin exist. (Almost all lignin by-products of pulping processes are burned and most of the heat generated from the lignin is required to evaporate the water from the spent liquor).
15. Crude alkali lignin and lignosulfonate products have been used as emulsifiers, protective colloids to stablize emulsions, in ore flotation, electrolytic refining, and industrial water treatment. Sequestering action is used to remove scums and insoluble salts in hard water. Lignosulfonates react with chromates and dichromates to give strongly insoluble materials.

PRISTINE LIGNIN: NOVEL TREATMENT POLYMER

Molecular Properties

The molecular weights reported for lignin which is isolated by various methods, vary considerably. Such studies have been made on soluble lignins and on lignin derivatives by a variety of methods. Values ranging from 300 to 140,000 have been reported. The molecular size of any given preparation depends upon the degree of degradation occurring during its isolation and/or its condensation into larger molecules. Thus, the conditions of isolation have a pronounced effect on the molecular size and polydispersity of a given sample. The molecular weights reported for soluble lignins are usually between 800 and 10,000 (3,4).

Despite the property of "solubility" discussed above, lignin is complex and should not be thought to exist as a uniform compound. *In toto*, it exhibits a three-dimensional crosslinking or network, gel properties, a colloidal nature, and adsorbent properties. Consequently, there is an inherent flexibility in isolating or preparing grades, as it were, of lignin which meet various application criteria. Lignin was expected to adsorb a variety of substances from the gaseous or liquid phase, with swelling in some cases. The variability in behavior of lignin supports the view that lignin isolates may exist as a three-dimensional network, capable of sorption and some swelling, but not as a true solution.

Adsorbent Applications

The focus of this research was concentrated on the use of lignin as an adsorbent and a replacement for activated carbon.

The use of pristine lignin, as a low-cost adsorbent, relies on effective chemisorption and physical adsorption and its disposability as a combustible material or by biological degradation, e.g. with white rot fungi. The material was expected to attenuate heavy metals and organic compounds in a mechanism similar to that of humic acids in nature. A critical factor would be the development of high surface area in the lignin. The pristine lignin was normally produced in powdered form and must be mixed with wastewater for several minutes to allow adsorption to occur prior to removal by settling or other methods. Powdered lignin was likely to be cheap enough to require minimal, if any, regeneration. The use of lignin in place of activated carbon would allow the reduction of energy costs associated with carbon adsorption and regeneration. Approximately 120 kwh electricity and 3.3 million BTU of fuel are used per 10^6 gal of wastewater processed and 1.5 million BTU's of energy per million gallons of wastewater is required to manufacture activated carbon to make up for carbon lost in regeneration. At 10 mgd, the costs of carbon adsorption and regeneration are about 17-22 cents per 1,000 gallons while at one mgd, if carbon regeneration is not practiced, they may be as high as 42 cents per 1,000 gallons.

PROCESSING AND ECONOMICS

Pristine Lignin Production

Pristine lignin production is accomplished by the hydrothermal decompression of lignocellulosic materials. At least two commercial processes exist for accomplishing the task. One process, that of Iotech, Inc., involves batch steam explosion while the other, from Stake Technology Ltd., is a continuous process. Several cellulose-to-ethanol processes now call for pre-separation of the lignin in woody biomass from the carbohydrate fractions. Investigators at Georgia Tech demonstrated that pre-separation of lignin followed by hydrolysis of cellulose in a plug flow reactor, with recycling, allowed conversion rates to sugar of 80% as contrasted with the limiting conversions of 55% obtained in conventional acid hydrolysis processes and that pristine lignin is readily isolated at low energy levels and for low cost. (2a-g).

Using the GIT process (Figure 2) for purposes of discussion, lignin separation can be illustrated. The process starts with steam explosion pretreatment using a Stake Technology reactor. Wood chips are subjected to high pressure steam and then explosively decompressed. Pilot scale studies conducted at Georgia Tech used a one-ton per hour Stake Technology reactor. We found that sufficient disintegration of the wood structure

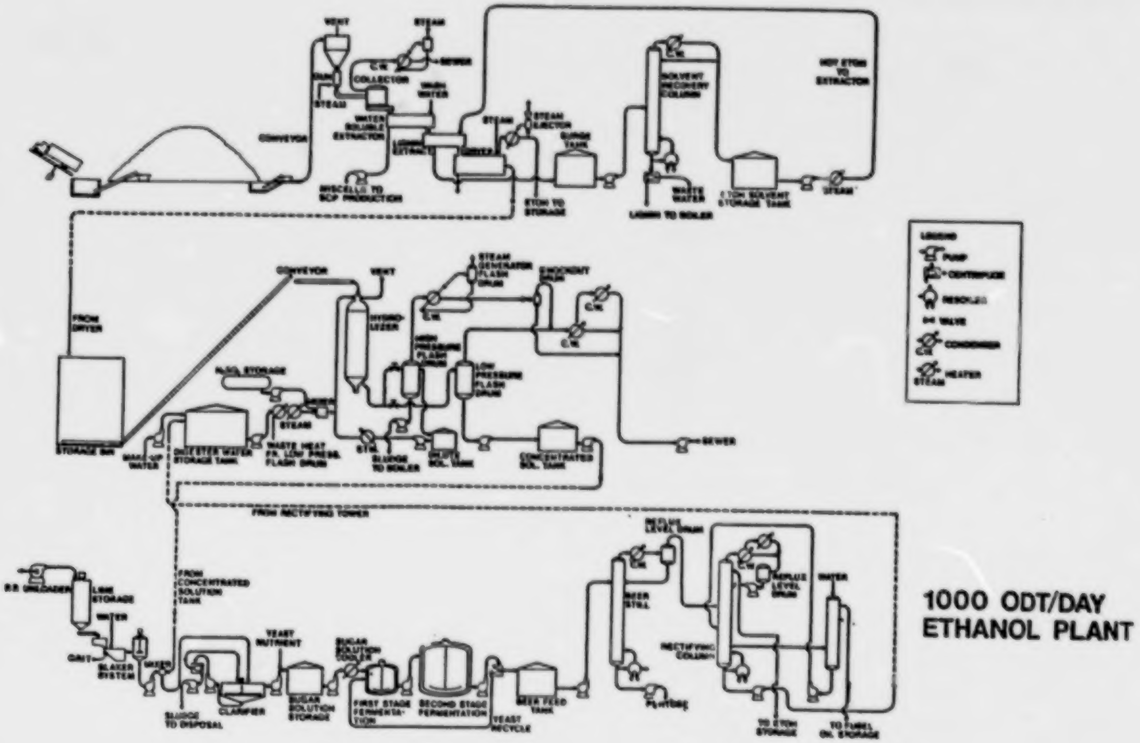


FIGURE 2. THE GIT PROCESS

occurred at 300-350 psig to facilitate removal of 90% of the original lignin. The Iotech process specifies at least 600 psig steam to achieve comparable results.

Several process improvements have been made for the facile isolation of lignin under relatively mild conditions and with modest capital investment being required. In our initial design extractors were specified for removing water- and alcohol-soluble components following steam explosion. These procedures were not optimized for lignin isolation but for cellulose isolation. Pilot plant studies have indicated that water and dilute alkali washing to remove these same components can be adequately performed on a continuous horizontal vacuum filter. Apparently the water-soluble organics and lignin are deposited on or near the surface of the steam-exploded wood. Hence, they are readily dissolved and separated from the wood as filtrate.

Originally a hot aqueous solution of 50% ethanol was specified for extracting lignin. In this case the ethanol had to be diluted to precipitate the lignin and then concentrated to recover the ethanol. Despite incorporating an ethanol recovery process, significant losses of ethanol are expected. Dilute caustic, 0.4%, at room temperature is a more effective solvent for lignin and, due to its modest cost, the caustic does not need to be recovered. The lignin is precipitated by neutralizing the caustic with sulfuric acid. Both the capital and chemical requirements are reduced by using dilute sodium hydroxide extraction and the amount of lignin removed is increased.

In the economic analysis of the GIT process, the selling price of ethanol produced from a 1,000 oven-dry ton per day plant was costed on two bases. Conservatively, all the major by products, including lignin (1.6 cents per lb) are used as fuel. This worst-case estimate gave a price of $2.28 per gallon of 95% ethanol which is 25% above the then current price ($1.80) of commercially available ethanol. However, when taking account of current values for furfural and acetic aid and assigning a value of six (6) cents per lb for lignin (set equal to the market price of sodium lignin sulfonate), the net selling price for 95% ethanol drops to a startling $1.08/gallon.

One may conclude that the development of a major application for pristine lignin will assure the development of major markets for the products of integrated wood/biomass-to-chemical/fuels processes.

One may conclude also that the selling price or cost of lignin will be no less than 1.6 cents per pound and be no greater than 6 cents per lb. In this price range, lignin is an extremely inexpensive raw material for virtually any application. Considering that it is already a tractable polymer or pre-polymer (if one were to make derivatives) it is noteworthy that it is only 10-20% the cost of simple monomers, such as phenol (30-50 cents per pound). Consequently, its potential for production of low-cost ion exchange resin derivatives is great.

Conceptual Design and Process Economics: Sample Case

The cost advantages to be derived from the use of pristine lignin depend on the mode of application, i.e., as an adsorbent, as an ion-exchange resin, or as a precipitating agent or coagulant. Its advantages will differ depending on the process or materials to which it will be compared.

Table 2 Design Criteria and Cost Calculations for a 1 MGD Liquid Waste Treatment Plant

Systems & Design Criteria	Design Parameter	Construction Cost *	Operating Parameter	Energy KWH/Yr	Maint. Material ($/Yr)	Labor hr/yr
In Plant Pumping, 60' hd	1.5 MGD	31,000	1 MGD	90,000	350	520
Pressure Adsorbers	3 X 1000 ft^3 contractors	350,000	3000 ft^3	96,000	1300	700
Initial Adsorbent Charge 26 lb/ft^3	80,000 lb					
Backwash Pumping - 18 gpm/ft^2	1250 gpm	43,000	140ft^2	3,400	400	150
Washwater Surge Basin (Plastic liner)	20,000 gal	10,000				
Liquid Waste Surge	150,000 gal	50,000				
Treated Effluent	40,000 gal	14,000				
Gravity Filtration - 5 gpm/ft^2	140 ft^2	171,000	140 ft^2	44,000	820	960
Filter Media - Mixed	140 ft^2	9,000				
Analytical Lab Trailer & Equipment	200 ft^2	25,000		60,000	2000	2000
Administrator Trailer	200 ft^2	25,000		40,000	1000	1000
		728,000		333,400	5780	5330

(Continued)

Table 2 (continued)

Site Preparation @ 5% (Excluding Adsorbents)	36,400
Total Construction Costs (Less Adsorbents)	764,000
General Contractor's OH & Profit @ 10%	76,400
Subtotal	840,800
Engineering @ 10%	84,100
Subtotal	924,900
Interest during design and construction - 7%	64,800
Total Capital Costs (1979)	989,700
Assume Cost Index = 1.50	
Estimated Total Capital Costs (1984)	$1,485,000

* A 10% on cost was included for skid mount unit (All Costs were based on 1979 Figures).
Reference EPA 600/2-79-162 a-b, August 1979

For purposes of this study a conceptual design and cost estimate was prepared for the use of pristine lignin as an adsorbent for a one million gallon per day (1 MGD) liquid waste treatment plant. The process flow diagram is presented in Figure 3 and the cost estimate in Table 2 and 3. It should be noted that annual operating costs do not include cost of adsorbent. From the design, it will be apparent that lignin provides several cost advantages over, for example, the use of carbon adsorption:

a. Assuming lignin will be disposed after saturation and that it will be incinerated with or without recovery of metals, the capital expense associated with regeneration and recycling of activated carbon is eliminated.

b. Lignin is substantially cheaper than activated carbon, ion-exchange resins, and is even more inexpensive than the common inorganic coagulants (5). See Table 4.

Table 3 Annual Cost for a 1 MGD Adsorption Plant

Item:	Total Costs/Yr.
Amortized Capital @ 7%, 20 yrs.	94,000
Labor, 5330 hr. @ Avg. $12/hr. (including fringe & Benefits)	63,960
Electricity, 333,400 KWH @ $0.03	10,000
Maintenance Material	5,780
Total Annual Cost* (1979)	$174,140
Assume Cost Index = 1.50	
Total Annual Cost (1984)	$261,200

*Cost estimate is based on August 1979 prices and excluding costs for lignins and lignins disposal (mainly incineration)

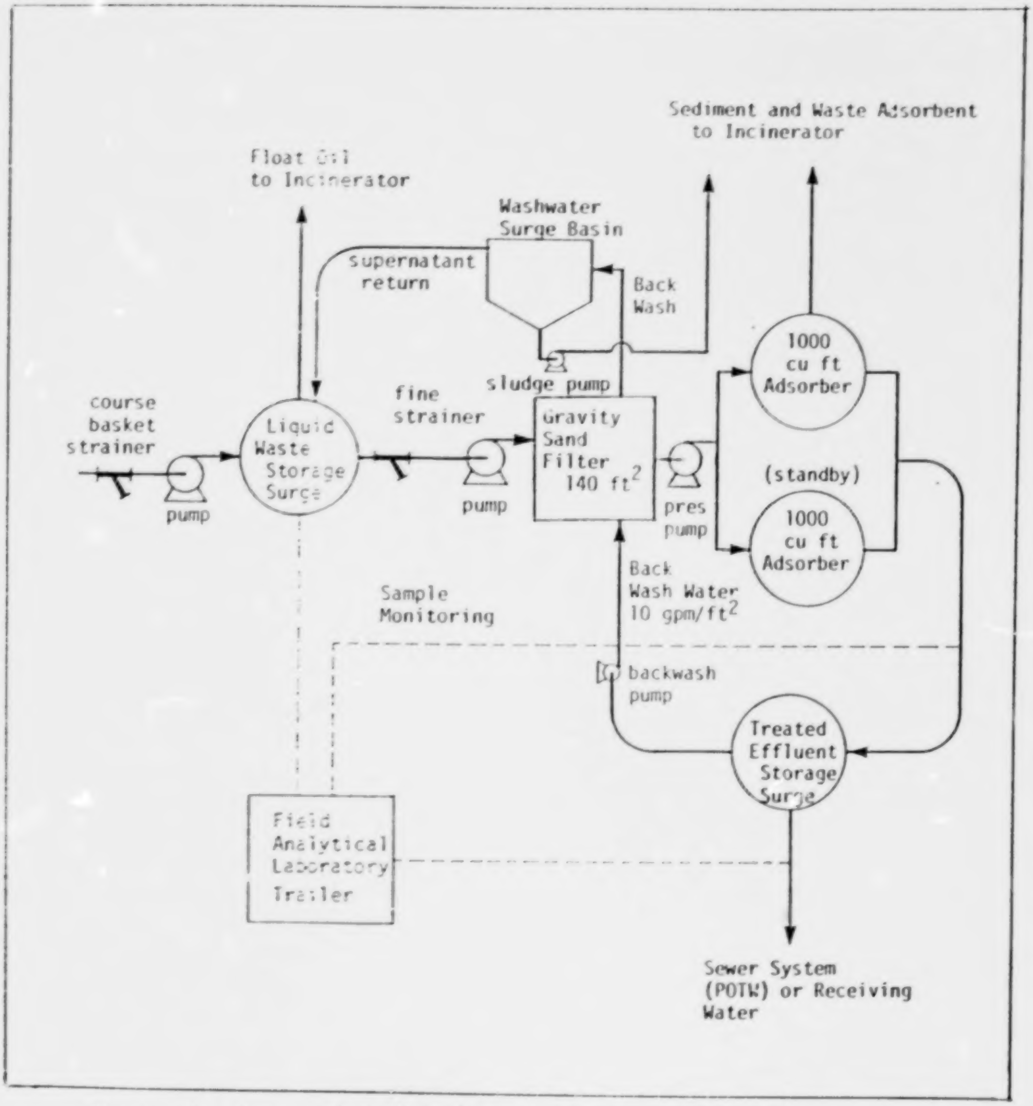

Sediment and Waste Adsorbent to Incinerator
Float Oil to Incinerator
Washwater Surge Basin
supernatant return
Back Wash
1000 cu ft Adsorber
sludge pump
course basket strainer
fine strainer
Liquid Waste Storage Surge
Gravity Sand Filter 140 ft²
pump
pump
pres pump
(standby)
1000 cu ft Adsorber
Back Wash Water 10 gpm/ft²
Sample Monitoring
backwash pump
Treated Effluent Storage Surge
Field Analytical Laboratory Trailer
Sewer System (POTW) or Receiving Water

Figure 3 Conceptual Design of a 1 MGD Treatment Plant

Table 4 Costs of Lignin and Alternatives

Water Treatment Chemical	Cost
Activated Carbon	$1.19/kg
Ion-exchange resins	2.87/kg
Coagulants	0.20/kg
Lignin (fuel value)	0.03/kg
Lignin (as ligniosulfonate)	0.13/kg

The EPA estimates that, without regeneration, carbon adsorption costs as high as $0.42/1000-gallon for a one MGD plant, i.e. an annual costs of $153,000. Since the bulk density of Filtrasorb 300 and 400 activated carbon averages 433 kg/cu.m. and pristine lignin ranges from 336 kg/cu.m. (ethanolic) to 600 kg/cu.m. (alkaline) adsorbent vessels should be similarly sized and, therefore, capital costs should be approximatley the same. The comparable cost for use of lignin at different levels of comparative efficiency follows, using a median cost-price of 8 cents/kg (halfway between fuel value and sodium lignin cost). The costs are applied for our conceptual design in Table 5.

Table 5 Comparison of Lignin Costs at Various Efficiency Levels Relative To Activated Carbon

Lignin Efficiency	Metric Tons Required	Annual Materials Cost
Twice as efficient	64	$ 5,120
Equal efficiency	128.5	10,280
1/2 efficiency	257	20,560
1/4 efficiency	514	41,120
1/10 efficiency	1285	102,800
1/15 efficiency	1928	154,000
Activated Carbon	128.5	153,000

If one were to proceed in a similar manner to compare lignin with ion-exchange resins, well-over a twenty-fold raw material cost advantage is possible on a simple equivalency basis.

SECTION 2

CONCLUSIONS

1. If the surface area of pristine lignin isolates could be substantially increased, they are potentially competitive with activated carbon on a cost-effectiveness basis for adsorption of polar compounds among priority pollutants.

2. The adsorption capacity of alkaline-isolated lignin for heavy metals (chromium and lead) is approximately equivalent to that of activated carbon (9 g/kg vs. 28 g/kg) despite a huge divergence in surface area (0.1 m^2/g vs. 1000 m^2/g). The applicability of pristine lignin for polishing of heavy metal wastewater is suggested with little further modification being required.

3. The adsorption capacities (for model organic compounds) of specific lignin isolates, which were examined in this study, were less than those of activated carbon and they failed to achieve the 1/15th-to-1/20th value of carbon adsorption capacity (Although phenol results approached the criterion) which has been targeted as a technical and economic break-even criterion for comparability of lignin and activated carbon. The adsorption capacities for phenol under comparable conditions with activated carbon and pristine lignin, were 46 g/kg and 1.6g/kg, respectively. Corresponding adsorbent loads were 100 mg/l and 3000 mg/l, respectively. Naphthalene was adsorbed by lignin, but the disparity was greater. Only marginal adsorption of

trichloroethylene was evident and there was a general insensitivity to increased adsorbent load for this purgeable compound.

4. The major impediment to achievement of comparability on technoeconomic grounds by lignin with activated carbon is attributed to the inordinately low values of surface area (order of 0.1 m^2/g for alkaline-isolated lignin). In general, adsorbents used in commercial adsorption processes exhibit high surface area per unit of weight (100-1000 m^2/g).

5. Another significant impediment to the realization of higher adsorption potential of lignin appeared to be the state of extensive substitution of the aromatic nuclei in the macromolelcular structure and a high methoxyl group content (vis-vis phenoxy hydroxyl content). Since experiments were conducted with a single source of steam-exploded wood processed under a fixed set of conditions (350 psig, 4 minutes), the nature of the lignin in the starting material was itself fixed, i.e. there was no flexibility in varying or modifying the composition of the lignin isolates which were studied, other than in the fraction of the lignin component which was extractable (8% for ethanolic lignin and 32% for alkaline lignin). If conditions could be optimized during steam-explosion (autohydrolysis), methoxyl groups could be "uncapped", increasing phenolic hydroxyl content and/or establishing a higher quinonic character, with the possibility of greater electron delocalization, hydrogen bonding, and other secondary bonding forces becoming operative during adsorption of polar compounds.

6. The surface activity of lignin isolates, though seriously limited to the available active sites on a very limited surface area, did show a preferred affinity for phenol and chromium (and to a lesser degree, for naphthalene) which is indicative of a highly polar adsorption mechanism at the surface. The magnitude of such effects should be enhanced by the induction of micro- and macro-porosity in the lignin isolates.

7. The adsorption kinetics study revealed relatively rapid equilibrium of heavy metals by alkaline lignin suggesting primary bonding forces at work, probably via a cation exchange mechanism involving residual sodium ions and the carboxylate or phenolate anions of the lignin macromolecule. (In these studies alkaline lignin (60x100 mesh) removed 91% of the original chromium concentration and 80% of the lead ion concentration. Despite a higher surface area, ethanolic lignin isolates did not perform as well: 52% and 42% for chromium and lead removal, resp.).

8. The adsorption isotherm curves, developed for the Freundlich isotherm equation, were of the S-1 type (Giles classification). The behavior is explained by the force of interaction between adsorbed molecules being significant relative to that between solute and adsorbent. Solute molecules tend to be packed in rows or clusters on the surface and the condition is encouraged with water as solvent, which itself is strongly adsorbed on a polar absorbent (lignin) and when the solute is mono-functional (as with phenol).

9. The experimental evidence in toto suggests that it would be premature to conclude that pristine lignin cannot be developed further to be a low-cost, efficient adsorbent

for polar organic priority pollutants or a cost-competitive and effective ion-exchange resin for heavy metal hazardous waste treatment. As an adsorbent, its thermal characteristics (higher heating value of over 11,000 BTU/lb. strongly suggest its disposability thermally. Alternatively, biochemical (fungal) degradation may be used alternative. In both disposal cases, the hazardous wastes would be concentrated.

SECTION 3

RECOMMENDATIONS

Despite the limitations of time and resources which are associated with feasibility studies such as this one, there appears to be ample evidence that lignin which is isolatable from steam-exploded wood, when the latter material is itself processed to optimize the extractability quantitatively and qualitatively of the modified lignin possesses the potential of being either a low-cost, high-efficiency adsorbent for polar compounds which is competitive with activated carbon or a precursor for a highly-efficient ion-exchange resin for clean-up of heavy metal ions.

A Phase II study is recommended with the objective of producing a steam-exploded or autohydrolyzed hardwood under operational conditions whereby lignin can be chemically debonded from the carbohydrate (cellulose and hemicellulose) components of wood in such a way that it is readily extracted in high yields and in a chemical form in which deleterious condensation (lignin-lignin or lignin-carbohydrate secondary reactions) is minimized and in which phenolic hydroxyl and quinonic content is maximized. In addition, the lignin should be isolated, preferentially, by chemical process operations which provide surface area of in the region of 100-1000 m^2/g. The surface area enhancement may be achieved by one or more of the following techniques.

(a) mild crosslinking associated with "blowing agents"
(b) controlled sol-gel techniques
(c) spray drying
(d) uniform coating of low-cost inert supports (with or without subsequent removal of supports)
(e) optimized solvent-nonsolvent precipitation systems

In a parallel study, the pristine lignin isolate would be directly compared to commercial weak-acid and cation exchange resins. Also, with modification, because of the highly aromaticized structure, derivatives of pristine lignin representative of the major classes of ion-exchange resins will be prepared since the low cost of the lignin isolate (e.g., 5-6¢/lb for phenol) allows derivatives to be highly cost-competitive with the expensive commercial synthetic ion-exchange resins (e.g., $3/kg)

In summary, the following study elements are proposed:

(1) Investigate/identify preferred conditions for steam explosion or autohydrolysis to produce preferred chemical structure in the lignin isolate.

(2) Qualitatively characterize lignin isolates to enhance the basic chemical structure (a) for preferential adsorption of polar hazardous waste compounds and (b) for facile modification of the structure to produce ion-exchange resins.

(3) Maximized yields of extractable lignin from steam-processed hardwoods.

(4) Develop a (preferably one-stage) process for production of high surface-area (100-1000 m^2/g) lignin isolates with minimal mitigation of surface activity.

(5) Perform kinetics and adsorption isotherm studies with selected model polar compounds drawn from the USEPA list of priority pollutants using both modified lignin isolates and activated carbon.

(6) Prepare chemically-modified lignin derivatives for use and evaluation as ion-exchange resins for the clean-up of heavy metal pollutants (and anions, possibly). Minor modifications include possibilities of (a) oxidation to increase acidic, phenolic, quinonic, ketonic, or aldehydic content and (b) increasing crosslink density/gelation through thermal or thermo-chemical treatments. Major modification involves chemical substitution, for example, of the aromatic nuclei or preparation of strong-base, anion-exchange resins by chloromethylation followed by reaction with a trialkyl amine.

(7) Characterize the modified lignin ion-exchange resins as to their porosity, surface area, ion capacity, volume stability, swelling, etc.

(8) Prepare a final report on the benefits, technical and economic, of employing lignin as an adsorbent or as an ion-exchange resin for hazardous waste treatment.

Section 4

MATERIALS AND METHODOLOGY

The experimental program consisted of three principal phases, viz.

(1) Isolation of pristine lignin from steam-exploded wood

(2) Chemical and physical characterization of lignin from steam-exploded wood

(3) Adsorption behavior of pristine lignin with selected model hazardous waste compounds

QUALITY ASSURANCE AND QUALITY CONTROL

In order to ensure the quality of analyses of the same substances and comparability within known statistical limits and with other analysts at different places and different times, quality assurance and quality control have been carried out throughout the whole study.

Quality Control (QC) includes all of the steps taken in the laboratory to control all measurement systems exployed in the study, insofar as possible so that they will be calibrated and accounted and that they will remain so in ensuing analyses.

Quality Assurance (QA) includes all the means taken within or beyond the lab to make certain the measurement systems in a monitoring network remain in calibration with an external standards, hence with other labs.

To do this, a QA/QC plan was set up from the very beginning of the project. It included the following aspects:

1. Project description
2. Project organization and responsibility
3. QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness and comparability
4. Sampling procedures
5. Sample custody
6. Calibration procedures, references and reporting
7. Analytical procedures
8. Data reduction, validation and reporting
9. Internal quality control checks
10. Performance and system audit
11. Preventive maintenance
12. Specific routine procedures used to assess data precision, accuracy and completeness
13. Corrective action
14. QA assurance reports to management

A revised Quality Assurance Project Plan submitted in the first quarter of the project was approved. No deviations, except as infrequently noted in quarterly reports, were required and these were all a direct consequence of the lack of direct applicability of established procedures to a substance as complex as lignin.

ISOLATION OF PRISTINE LIGNIN FROM STEAM-EXPLODED WOOD

Efforts were focused on obtaining pristine lignin in a physical (solid) form which is facilely isolatable and which would present a relatively pure, consistent, and light free-flowing powder (ultimately of prescribable dimensions). Two primary sources of lignin were used in this study.

The first source of steam-exploded wood was produced at Georgia Tech from the hydrothermal decompression of Tulip (or Yellow) poplar, Liriodendron tulipifera, chips at a steam pressure of 350 psig and a residence time of four (4) minutes using a Stake Technology, Ltd. continuous digester rated at one ton per hour. (1) (Note: Tulip poplar is a relatively fast growing hardwood and is abundant in the southeastern United States). Only lignin isolated from the source was used to conduct adsorption studies.

The second source of steam-exploded hardwood was a twenty (20) kilogram sample of Aspen hardwood (Populus tremuloides) provided by Stake Technology, Ltd. in Canada (2) which reportedly was produced at a steam pressure of 315 psig for four (4) minutes.

Preliminary Isolation Experiments

Four lignin batches were prepared using slightly differing extraction and precipitation methodology for each batch. The wood stock used was steam-exploded Tulip poplar and the solvent was 95% ethanol.

The first three extractions (SH-015, SH-016, SH-017) were performed to improve extraction and lignin recovery procedures and were semi-quantitative. The moisture content of the Tulip poplar was estimated to be 40-65% by weight for SH-016 and SH-017.

The fourth extraction (A-005-7) used quantitative precipitation methodology and was modified to effect a flocculant precipitate.

SH-015 Isolation

A small scale trial extraction of steam-exploded wood was performed using absolute ethanol as an extractant. Extraction proceeded for about 8 hours. The volume of extract was reduced by rotary evaporation of the solvent. Various ratios of ethanol extractant solution to the non-solvents, water and benzene, were investigated to evaluate the physical character and general filterability of the lignin precipitate. Water was determined to be a better non-solvent than benzene as a more filterable and stable precipitate was obtained. Benzene-precipitated lignin changed from a particulate state to a gum on standing before separation. Approximately 5g of a dry, light brown, powdery material was obtained from aqueous precipitation after drying and vacuum drying steps. Recovery was low and no yield was determined.

SH-016 Isolation

Approximately 2.5 liters of absolute ethanol was used to extract 503g of undried steam-exploded Tulip poplar. An air pocket formed in the base of the sample chamber of the Soxhlet extractor, interrupting the semicontinuous extraction. The experiment was stopped after 10 hours. The volume of the ethanol extract was reduced to about 300ml by rotary evaporation. During the rotary evaporation process the temperature reached 80°C or more for an undetermined amount of time. The solvent was evaporated by heating under vacuum to 45°C over several days. The resulting residue had a mass of 19.5g (dry) and was a dark brown, friable powder. An approximate yield of 15% was estimated. The effects of "overheating" during work-up was reflected in differences in infrared spectra.

SH-017 Isolation

Approximately 2.3 liters of absolute ethanol was used to extract 328g of undried, steam-exploded Tulip poplar. The Soxhlet extraction was run for about 24 hours. The extract volume was reduced with gentle heating (<50°C) and rotary evaporation. This sample was not precipitated. Solvent was evaporated by heating at 45°C under vacuum for several days. The resulting residue was a dark brown, friable material with a mass of about 8.0g. A precise per cent yield could not be determined as the initial water content was not determined. Recovery efficiency was probably less than 25% of the available lignin.

A-005-7 Lignin Isolate

Approximately 1kg of steam-exploded Tulip poplar stock was dried by heating in a convection oven at 90°C for 48 hours, then dried under vacuum at 110°C for 6 hours. The "dry" material was sealed in a plastic bag. An aliquot was taken and maintained at 110°C for 24 hours; the measured volatile content was about 4.4%. The "dry" stock remained in the plastic bag at ambient conditions for about 48 hours prior to extraction.

About 500g of "dry" material was removed for lignin extraction. About 110g was saved for moisture determination by the TAPPI-208-M-84 method. The water content was determined to be 18% by this method. A sample of this steam-exploded Tulip poplar (408g) of 18% (w/w) water was taken for Soxhlet extraction of lignin using a 95:5 ethanol/water solution. Ethanol and water forms an azeotrope composed of 95.6% (w/w) ethanol and 4.4% (w/w) water with boiling point 78.2°C and this solvent system was evaluated as lignin is reported to be more soluble in the aqueous ethanol than in absolute ethanol. Approximately 4.5 liters of solution was used for the extraction which was allowed to continue for 72 hours. Samples were taken at 2 hours, 48 hours and 72 hours for infrared analysis; no differences were noted in functional groups. It was necessary to add 400-500ml of solution to the flask at about 24 hour intervals. The final total volume was 3-3.5 liters of lignin solution.

This solution was vacuum evaporated using a rotary evaporator; temperature was maintained at 40°C. The volume was reduced to 480ml. This concentrated solution was split into three fractions for evaluating alternate precipitation techniques. The lignin concentrate was added dropwise to the vortex of a stirred aqueous solution.

A-005-7-1: 140ml of lignin concentrate was precipitated in an aqueous HCl solution of pH = 1-2. A flocculant precipitate was obtained which was more more filterable than in earlier experiments. The supernate was a claret color. The filtrate was water-washed twice, air-dried for 48 hours, and then vacuum dried at 45°C for 24 hours. A dark brown, friable material (suggesting HCl induced degradation?) was obtained with a dry weight 2.54g.

A-005-7-2: Approximately 200ml of lignin concentrate was precipitated using an aqueous H_2SO_4 solution of pH = 4-5. A flocculant, "clumpy", readily filterable brown precipitate was formed which showed relatively rapid settling behavior when stirring was stopped. The supernate was a claret color. The filtrate was water-washed twice, air-dried and vacuum-dried as described previously. A light brown, powdery material was obtained with a dry weight of 18.3g.

A-005-7-3 and A-005-7-4: These isolates were obtained from approximately 140ml of lignin concentrate precipitated in distilled/deionized water of pH = 5.6 by two different procedures, respectively. Grainy brown precipitates were formed with the supernates being colored yellow. A-005-7-3 was obtained by adding water to the lignin concentrate. A-005-7-4 was obtained by adding lignin concentrate to water. No physical differences were apparent. Samples were allowed to stand for 24 hours before filtering. Very little settling occurred. The particle size was very small. The solids were separated using a Buchner funnel on filter paper and were water-washed once, resulting in an apparent loss of material through the filter paper. The isolated samples were air- and vacuum-dried as described. A light brown powdery material was obtained with a combined dry weight of 3.25g.

A-005-7-5: This isolate was a gummy residue which remained after rotary evaporation of the filtrates. This residue was washed from the flask with deionized water and dried as described. The dark brown, friable material had a dry weight of 0.84g.

A total of 24.9g of lignin was recovered from the initial 335g (dry) steam-exploded wood. Thus, combined "lignin" isolates representing 7.5% of the initial sample resulted indicating the need for improved extraction efficiency by improved recovery procedures, increased extraction cycles, improved solubility (solvents), avoidance of product decomposition, etc.

Ethanolic Isolates

Nine isolation experiments were conducted using 95% ethanol as the extractant.

In the case of experiments PH-045, PH-046, PH-047 and PH-048 the following procedure was used;

Three Soxhlet extractors were fitted with 5-liter boiling flasks and Friedrich condensers. Approximately 300 grams of steam-exploded wood was placed in each Soxhlet. Two (2) liters of 95% ethanol was placed in the boiling flask and 2.5 liters of ethanol was placed in the Soxhlet side-chamber. The temperature of the heating mantle was adjusted so as to achieve solvent reflux without vigorous boiling. The wood was extracted for 48 hours with approximately 25 cycles during this time. The extracts from each flask are combined and concentrated to one liter using a Buhli Rota-vapor. The concentrate is placed in an additional funnel and allowed to drip into 2.5 liters of water acidified with dilute sulfuric acid to pH 4-5. The dropwise addition is at a rate of 7 ml per minute. The insoluble lignin is filtered using a Buchner funnel fitted with Whatman No. 2 filter paper and water aspiration. This pristine lignin was allowed to air-dry to less than 5% moisture. The dried lignin was broken into pieces and then crushed using a mortar and pestle. The results reflect a yield from a combined sample weight of approximately 900 grams.

In the case of experiment PH042/043, the extracts from two parallel Soxhlet extractions were combined and worked up as just described. The yield of lignin reflects a sample size of steam exploded-wood of approximately 600 grams.

The earlier experiments (SH-038A, SH-038B, PH-040, and PH-041) represent extractions of approximately 300-350 gm. samples of the exploded Tulip poplar in single Soxhlet apparatus.

The "combination" experiments were practiced to produce sufficient quantities of a single-sourced lignin sample to allow adsorption studies to be performed comparatively.

Alkaline Extractions

A second series of extractions using NaOH were completed. Sodium hydroxide was added to 2500 ml of deionized water until the pH is 13. Approximately 225 grams of steam-exploded wood was added to this solution and stirred for 30 minutes. The extracted wood was initially filtered using a Buchner funnel fitted with filter cloth. This process was too slow, so the procedure was modified. The extracted wood was filtered using fluted paper with a fine 60 X 48 paint filter inside. The wood was then washed with four liters of deionized water. The lignin was precipitated by adding concentrated H_2SO_4 dropwise to the filtrate to adjust the pH to 1. The lignin was filtered using a glass funnel fitted with Whatman No. 2 fluted paper and a fine 60 X 48 paint filter. (Filtration with a Buchner funnel was attempted but found to be unsatisfactory due to amount of time required). The filtered lignin was allowed to air-dry. Final stage drying was accomplished in a vacuum oven at 60°C until constant weight was achieved. Typically, the alkaline isolate was a dark brown/black material contrasting with cream-colored ethanol-extracted lignin isolates.

A total of nineteen alkaline extractions were conducted with the GIT steam-exploded Tulip poplar. An additional thirty three alkaline isolations were conducted with the Stake Technology steam-exploded Aspen. The alkaline isolates are designated NaOH1 - NaOH19 and PSL1-PSL33, respectively.

Solubility Behavior

No comprehensive survey of solvent/non-solvent systems exists for pristine lignin polymers. Ethanolic solvents (aqueous) and dilute alkaline solutions have been found to be effective, although differing markedly in their yields, i.e. recovery of lignin from steam-exploded wood. Preliminary experiments showed that lignin "precipitate" (from certain solvent/non-solvent systems, e.g., ethanol/benzene) were metastable in that the apparent solid would change to an oily state on standing or on progressive addition of a lignin solution to the non-solvent. This was explicable in terms of progressive resolubilization of the lignin in a changing (compositionally) solvent/non-solvent systems. In order to identify, alternative solvent/non-solvent systems for the production of optimal modifications of lignin in future studies a solubility analysis was conducted.

A variety of conventional solvents or solvent mixtures was selected based on (a) their values of solubility parameter and (b) their hydrogen bonding index. The solubility of ethanol-extracted lignin isolate (PH-040) in various organic solvents was determined according to ASTM-D3132.

In a non-standardized procedure, lignin samples were added to the individual test tubes containing solvents and were (a) agitated by shaking and then (b) heated at 52°C for fifteen minutes to assess solubility. Some significant improvement in the rate of solubilization was noted with many solvents on agitation although little improvement was noted with a rise in temperature of the solvent from ambient temperature to 52°C (water bath). In a third series of solubility experiments, individual lignin isolates were reexamined as to their solubility, after isolation, in both 0.1N sodium hydroxide and 95% ethanol after standing 24 hours per ASTM-D3132.

In a fourth experiment, the solubility of the ethanolic lignin isolate and the alkaline lignin isolate used in the adsorption studies was evaluated in organic-free water after placing 250 mg of the lignin in 100 ml of the water and shaking for twenty-four (24) hours, followed by a Total Organic Carbon (TOC) analysis.

CHEMICAL AND PHYSICAL CHARACTERIZATION OF PRISTINE LIGNIN

Selected ethanolic - and alkaline-lignin isolates, as well as the steam-exploded wood feedstock were analyzed or evaluated by one or more of several analytical and test methods, procedures for which corresponded to a revised and agreed Quality Assurance Project Plan (QAPP) which was submitted in final form on 18 October 1985. No deviations, except as noted occasionally in quarterly reports, were required and these were a direct consequence of the non-homogeneous and complex nature of the material being characterized which necessitated some modification in established procedures.

The extensive characterization program included the following techniques:

1. Moisture determinations
2. Ash content
3. Klason Lignin Content
4. Elemental analysis (carbon, hydrogen, nitrogen)
5. Infrared spectroscopy
6. Ultraviolet spectroscopy
7. Nuclear magnetic resonance spectroscopy
8. Heat of Combustion
9. Differential scanning calorimetry
10. Thermogravimetric analysis
11. Electrochemical (Functional Group) Analysis
12. Gel permeation chromatography
13. Vapor pressure osmometry
14. BET Surface Area Analysis
15. Electron microscopy
16. Apparent density

Moisture Determinations

A series of moisture determinations of ethanol-extracted lignin was conducted. The QA plan originally called for the use of TAPPI-T208 for moisture analyses. However, this procedure required 100 gm of sample. With a limited supply of lignin isolates, the use of 200 gm of lignin per test (duplicate analysis) was not feasible. Consequently, both vacuum drying and Karl Fischer titration methods were assessed.

The vacuum drying technique provided the most consistent and reproducible results of the two methods and was adopted. In this procedure one gram of sample was weighed to the nearest 0.1 mg and was placed in a crucible which had been previously acid-washed and heated to 600°C, followed by cooling in a vacuum dessicator. The sample was weighed into the tared crucible and placed in a vacuum oven which had been heated to 60°C. The door was sealed and the oven was evacuated to a pressure of 25 in. Hg. The sample is weighed periodically until a constant weight was achieved. Typically, the time covered a period of seventy-two hours, with weighings made on a twenty four hour basis.

Ash Determinations

Ash content of lignin isolates was determined by ignition at 600°C to constant weight. The procedure guidelines are given in TAPPI Method T211 om-80.

Klason Lignin Content

The procedure for the determination of acid-insoluble lignin (Klason Lignin) used TAPPI Method T222 om-83, modified to exempt the ethanol-benzene extraction step which is inappropriate for steam-exploded wood (since the low molecular weight extractives found in untreated wood have already been removed and the solvent system would partially extract lignin, thereby producing lower values for the Klason lignin content in the steam-exploded wood).

Elemental Analysis (Carbon, Hydrogen, Nitrogen)

Elemental analyses were performed for each sample in duplicate using a Perkin Elmer Model 240°C with 3600 Data Station in-house (N.B. earlier analyses were conducted externally). The instrument was calibrated daily or before use using acetanilide

(P-E No. 0240-1121) as a standard. Standardization required approximately two hours. Samples were analyzed "as is" and results were corrected for residual moisture.

Infrared Spectroscopy

Infrared spectra were obtained on isolates by deposition of approximately twenty microliters of 0.1% (w/v) solutions in spectroquality tetrahydrofuran on 1 mm x 10mm AgCl disks. Raw spectra were corrected by ratioing with a blank AgCl blank spectrum. An average of three 3-minute scans were used. A Perkin Elmer 598 dual-beam infrared spectrophotometer with a Model 3500 data station was used, the instrument being calibrated with a standard polystyrene film of 0.05mm thickness (P-E Part No. 0457-5131).

Ultraviolet Spectroscopy

A Varian DMS-90 double beam ultraviolet spectrophotometer was used to record ultraviolet spectra. The instrument has a 2.0nm slit width and an X-Y chart expansion of 20 nm/cm. A scan rate of 50nm/min. was used. Lignin isolates were analyzed at 0.005% (w/v) concentration in spectroquality tetrahydrofuran.

Nuclear Magnetic Resonance Spectroscopy

Carbon-13 (^{13}C) NMR Spectra were run on alkaline and ethanolic isolates at ambient temperature (23°C) on a Varian XL-400 spectrometer operating with gated decoupling and double precision acquisition under the following conditions:

Solvent:	acetone or dimethylsulfoxide (DMSO)
Freqency:	100.576 MH_z
Pulse width:	9 and 77 degrees
Spectral width:	21978 H_z
Acquisition time:	0.364 sec.
No. of rep.:	3000
Approx. time:	3 hours
Spin rate:	25 H_z
Line broadening:	5.0 H_z
FT size:	16K

Heats of Combustion

Heats of combustion were determined in a Parr Model 1241 bomb calorimeter, with Model 1720 computer controller, operating in the isoperibol mode. The procedure was ASTM D32-86, "Gross Calorific Value of Solid Fuel By the Isothermal-Jacket Bomb Calorimeter." Benzoic acid pellets (Parr 3413), with a nominal weight of one gram, were used to calibrate the calorimeter.

Thermal Analysis

Temperature stability of lignin isolates was measured with a Perkin Elmer TGS-2 thermogravimetric analyzer which measures the weight loss (weight remaining as a % of initial weight) on dry samples of approximately 10 milligrams initially measured on an electronic balance (to 0.01-0.001 mg), over a temperature range from ambient to 400°C at a heating rate of 20°C/minute. The % weight change is recorded within limits of 0.01%. The TGS-L was operated with a Perkin Elmer Thermal Analysis Controller and Thermal Data Station which produce analytical results and data plots.

A Perkin Elmer DTA 1700 High Temperature Differential Thermal Analysis System, operated in the heat-flux mode for differential scanning calorimetry, with the same controller and data station used for the TGS-2, provided differential measurement of enthalpic transitions (mcal/sec.) and transition temperatures (°C) of lignin isolates versus an "inert" alumina powder over a range from ambient temperature to up to 300°C in air or in inert (nitrogen) atmospheres.

Electrochemical Analysis

The methodology developed for humic acids by E.M. Perdue et al (3, 4, 5) to analyze the behavior of organic acid functional groups (phenolic hydroxyl and carboxylic acids) upon electrochemical titration and to model the structural composition of the complex humic substances was adapted for application to lignin.

The apparatus employed follows:

(a) Teflon reaction vessel, sealed to exclude air, with a port for introducing a nitrogen blanket.
(b) pH electrode (Ross combination)
(c) Microburette equipped with an AC motor driven at 60 RPM.
(d) An IBM PC with software/interface for collection of pH data on disk and for control of titrant delivery

The reagents used were CO_2-free water, 2.0N NaOH, 2.0N HCl, and 0.98M KOH.

The procedure follows:

A 10 mg sample of lignin was dissolved in 80 ml of CO_2-free water. (Note: Samples of pristine lignin did not dissolve completely in CO_2-free water). The following procedure was modified to achieve dissolution. A volume of 1.5 ml of 2N NaOH was added to 80ml of CO_2-free water and sample. The sample then dissolved. Next 1.5 ml of 2N HCl was added to the solution and the sample was diluted to 100 ml in a volumetric flask). The dissolved sample was transferred to the Teflon reaction vessel, an N_2-purge was initiated and the titration was immediately initiated. For this procedure 0.98M KOH is used.

The pH was recorded and a volume of titrant was dispensed. The initial volume of titrant dispensed equaled one-fiftieth of the total volume specified by operator input to the computer. The pH of the solution was recorded after the titrant was dispensed when one of the following conditions was met:

(a) A standard deviation of less than 0.25mV (approximately 0.005 pH units) was achieved for 100 consecutive readings, taken at one second intervals or
(b) 400 readings were taken.

Therefore, after the pH was recorded and if the readings did not stabilize within 400 seconds, another increment of titrant was added, a minimum addition being 1.67 microliters. When the titration was completed a computer print-out of a table of pH readings vs. volume of titrant dispensed was produced.

The resulting experimental (pH vs. Organic Anion) data were fitted to the biomodal Gaussian distribution model of Perdue and coworkers (4, 5). The model describes the carboxyl and phenolic functional groups in an organic acid mixture as two classes of non-identical acidic functional groups. The acidity of carboxyl groups, for example, is thought to be attributable to a broad spectrum of acids with a range of pK values. The model determines the mean (most common) pK value (Mu), the "spread" of pK values around the mean value (Sigma), and the total concentation (Conc) of each class of acidic fuctional groups.

The following flow chart (Figure 4) outlines the computer program which was used to calculate the anion concentration. The calculation is based on a modified Debye-Huckel (Guntelberg) equation.

Gel Permeation Chromatography

Molecular weight distribution and analyses were conducted by gel permeation chromatography for the lignin isolates under the following conditions:

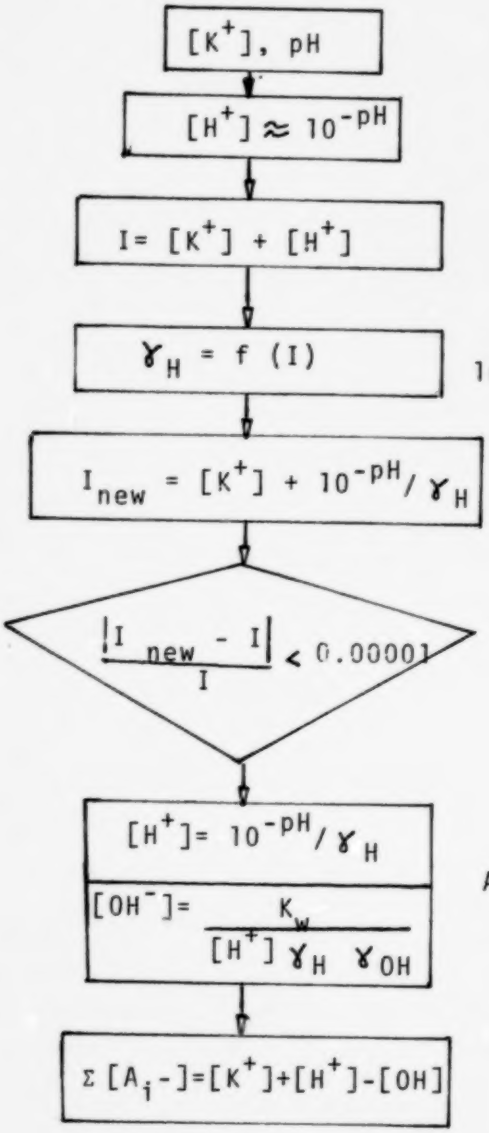
Instrument: Perkin Elmer Series 4LC with 3600 Data Station and Chrom 2 Data Acquisition System
Column: TSK GMH6 mixed bed column, 30 cm X 7.5 mm ID
Solvent: tetrahydroforan
Flow Rate: 1 ml per min.
Detector: PE LC85-UV detector @ 254mm and 0.64 AUFS

A calibration curve was prepared using these conditions with monodisperse polystyrene standards from Waters Associates and Polysciences, Inc. and with benzene. The calibration curve is given in Figure 5.

PROBLEM: How to convert pH to H^+ concentration and OH^- concentration, so that organic anion concentration can be calculated from:

$$\sum_i [A_i^-] = [K^+] + [H^+] - [OH^-]$$

$[K^+]$ is known from the amount of added KOH.



$[K^+]$, pH
$[H^+] \approx 10^{-pH}$
$I = [K^+] + [H^+]$
$\gamma_H = f(I)$
$I_{new} = [K^+] + 10^{-pH}/\gamma_H$
$\frac{|I_{new} - I|}{I} < 0.00001$
$[H^+] = 10^{-pH}/\gamma_H$
$[OH^-] = \frac{K_w}{[H^+]\gamma_H \gamma_{OH}}$
$\Sigma [A_i^-] = [K^+] + [H^+] - [OH]$

$$\log \gamma_H = \frac{-0.059\sqrt{I}}{1 + \sqrt{I}}$$

Assume: $\gamma_H = \gamma_{OH}$

FIGURE 4. FLOW CHART FOR CALCULATION OF ANIONS

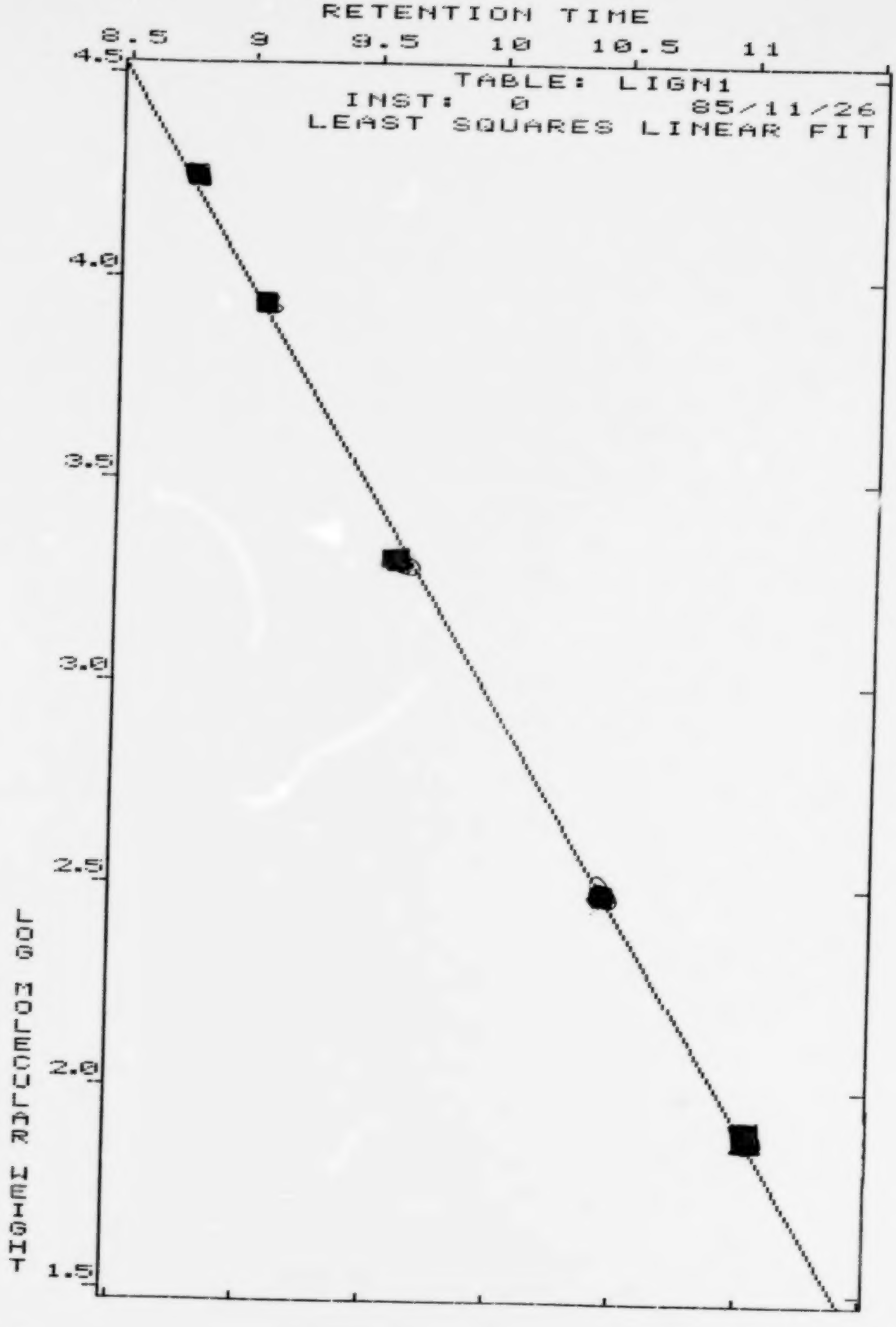


Figure 5 GPC Calibration Curve

BET Surface Area Analysis

Lignin samples were analyzed by Micromeritics for surface area determination using sample sizes of 1.0 - 1.5g (to 0.1mg), with nitrogen (for surface areas greater than one square meter per gram) or krypton (for surface areas less than 1 m^2/g) to develop adsorption isotherms at standard temperature and pressure (STP), and using equilibraton intervals of ten (10) seconds. The instrument was Micromeritics Digisorb 2600 and it is calibrated on a weekly basis with the following in-house reference standards:

Iron oxide	6.2-6.3	m^2/g
Anatase - TiO_2	10	m^2/g
Silica sphere	24.5	m^2/g
Carbon black	80-89	m^2/g
MIC820 (SiO_2-Al_2O_3 catalyst)	220	m^2/g

Scanning Electron Microscopy

The instrument used was a Cambridge 150 Stereoscan scanning electron microscope with Tracor Northern Model TN5500 energy dispersive X-ray spectrometer with back scatter electron and cathodoluminescence detector, quantitative software, and full-color video display unit. Samples were placed on SEM mounts with double-sided adhesive tape. A conductive layer of Au/Pd was sputter-coated on the sample before analysis. Magnifications typically were 100x to 200x.

Apparent (Bulk) Density

Apparent density for steam-exploded wood and lignin samples was conducted simply by weighing a sample of measureable volume in an appropriately-sized, tared and calibrated graduate with minimal agitation to arrive at an apparently-equilibrated volume. The technique is described in several ASTM methods for loose powders and solids.

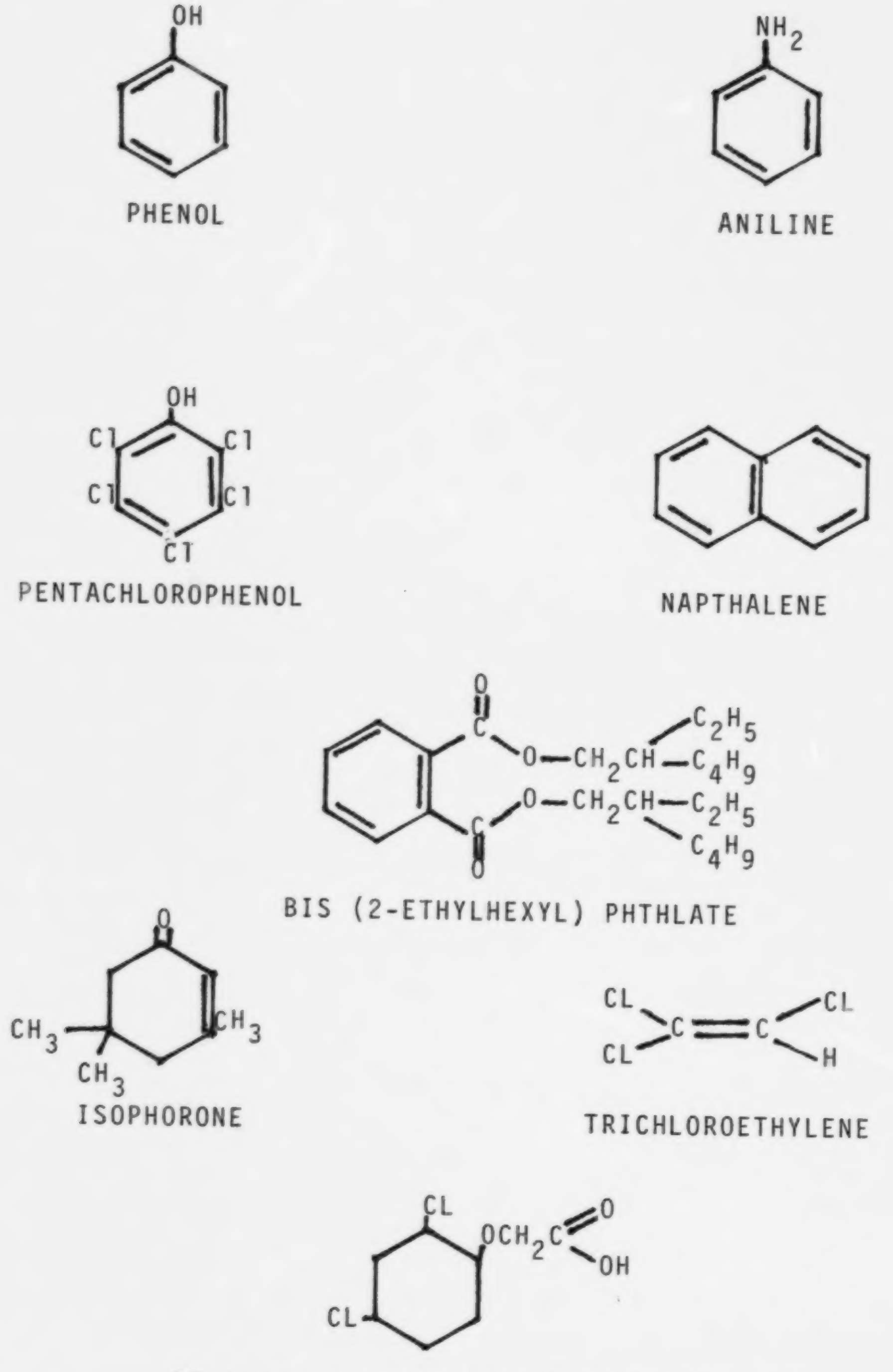
ADSORPTION BEHAVIOR OF PRISTINE LIGNIN WITH SELECTED MODEL HAZARDOUS WASTE COMPOUNDS

Adsorbates - Selection of Model Compounds

Ten (10) model compounds used in this study were aniline, phenol, naphthalene, isophorone, trichloroethylene, bis-(2-ethylhexyl)phthalate, pentachlorophenol, 2,4-dichlorophenoxy acetic acid, chromium and lead. These pollutants were selected based on the criteria as follows:

i) presence in municipal and industrial wastewater
ii) listed as hazardous waste or toxic under the Resource Conservation and Recovery Act (RCRA)
iii) representative of functional groups and a range of physical/chemical properties (base/neutral, acid extractable, purgeable organics, pesticide and heavy metals)
iv) amenable to current analytical methodology

The molecular structure of the eight organic compounds and their physical properties are shown in Figure 6 and Table 6.



PHENOL

ANILINE

PENTACHLOROPHENOL

NAPTHALENE

BIS (2-ETHYLHEXYL) PHTHLATE

ISOPHORONE

TRICHLOROETHYLENE

"2,4-D" 2,4-DICHLOROPHENOXYACETIC ACID

Figure 6 Molecular Structure of the Eight Model Organics

Table 6 Physical Properties of the Eight Organic Model Compounds*

Compounds and Formulas	Mol. Wt.	b.p. (°C)	m.p. (°C)	Solubility	kf.
Phenol	94.1	181.7	43	9300 (25) mg/L	1
C_6H_5OH				6700 (25) mg/1000 mL H_2O	2
Aniline	93.3	184	-6.3	3.7 g/100g of H_2O	
Naphthalene	128.9	218	80.5	(25°C) (25°C)	1
$C_{10}H_8$				30-34.4 mg/L	2
Isophorone $C_9H_{14}O$	320.35	214	--	al. eff. ace.	2
Bis(2ethylhexyl)phthalate $C_{24}H_{38}O_4$	390.56			(25) 50	1
Trichloroethylene	131.29	87	-73	(25°C) (20°C)	1
$ClCH = Cl_2$				1,000-1,100 mg/L	2
2,4-Dichlorophenoxyacetic acid $(2,4\text{-}Cl_2C_6H_3)CH_2COOH$	242.15	160	140	alcohol	
Pentachlorophenol	266	309-10	174	14 (20)	1
Cl_5C_6OH				20 (30)	2

* Data except solubility are adopted from "Handbook of Chemistry and Physics," 61st Ed., CRC Press. Solubility data are according to reference (14).

Analytical Methods - Organic Model Compounds

The analytical methods employed were based on the following USEPA Standard Methods

USEPA Method 604: Determination of Phenol and Certain Substituted Phenols

USEPA Method 606: Determination of Certain Phthalate Esters

USEPA Method 609: Determination of Certain Nitroaromatics and Isophorone

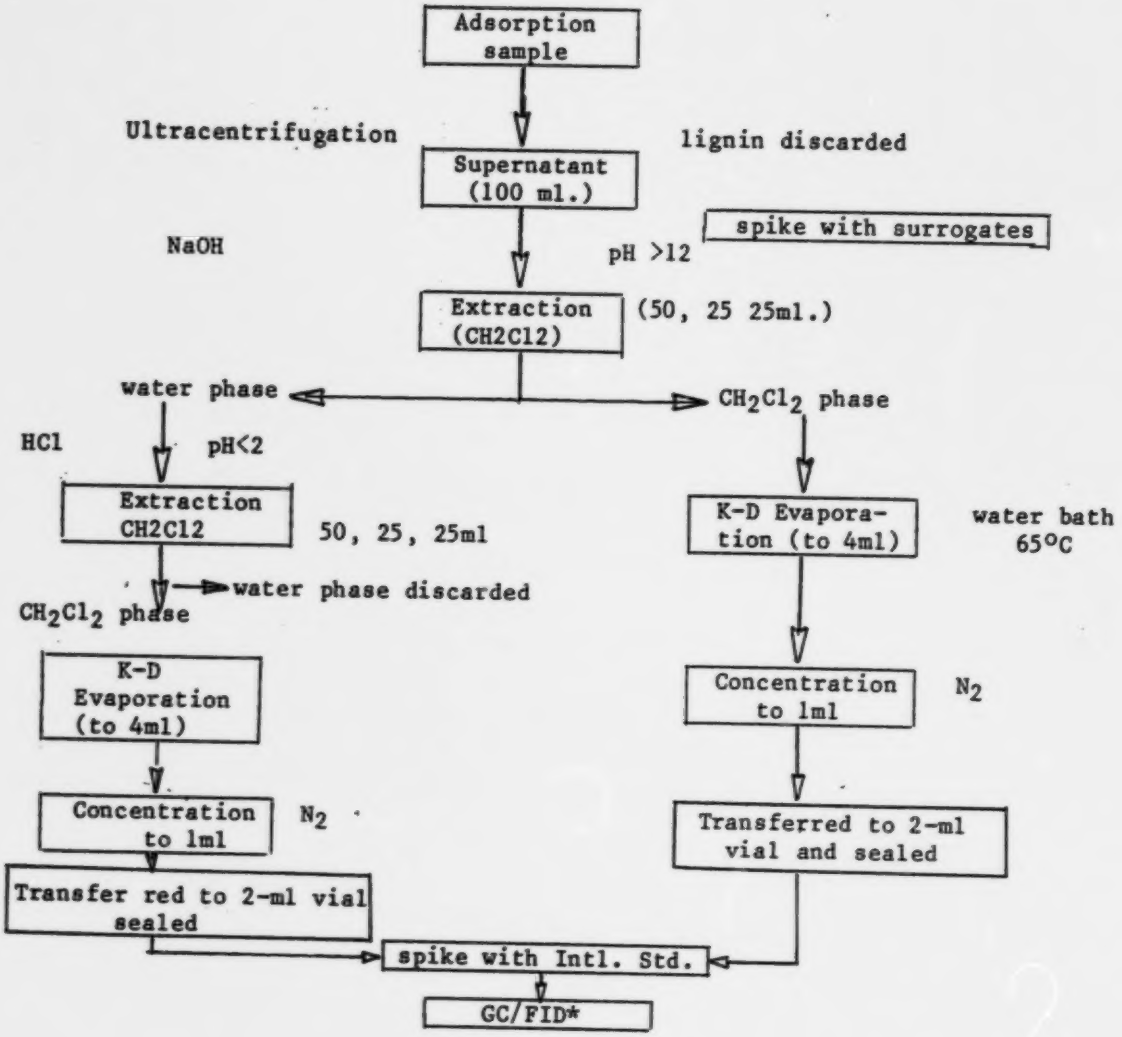
USEPA Method 304: Determination of Micro Amounts of Metals by Electrothermal Atomic Absorption Spectrophotometry

The schematic diagram of the analytical procedure employed for the analysis of the six-component extractable organic compound mixture is given in Figure 7. The analytical scheme for 2,4-D analysis was based on the method for chlorophenoxy acid particides in water and wastewater and the scheme is shown in Figure 8.

Trichloroethylene analysis was based on a liquid/liquid extraction method (water: n-pentane = 10:1). The following steps were involved (see Figure 9):

(1) The sample was collected in an 11.9 ml-volume glass vial which was sealed with an open screw cap fitted with a septum, lined with Teflon, through which a syringe needle may be inserted.

(2) The sample was spiked with a surrogate (1,1,-trichloroethane).



* Hp 5830 Gas chromatography
18850 GC Terminal and 7672A Automatic Sampler

Figure 7 Analytical procedures for Extractable organics

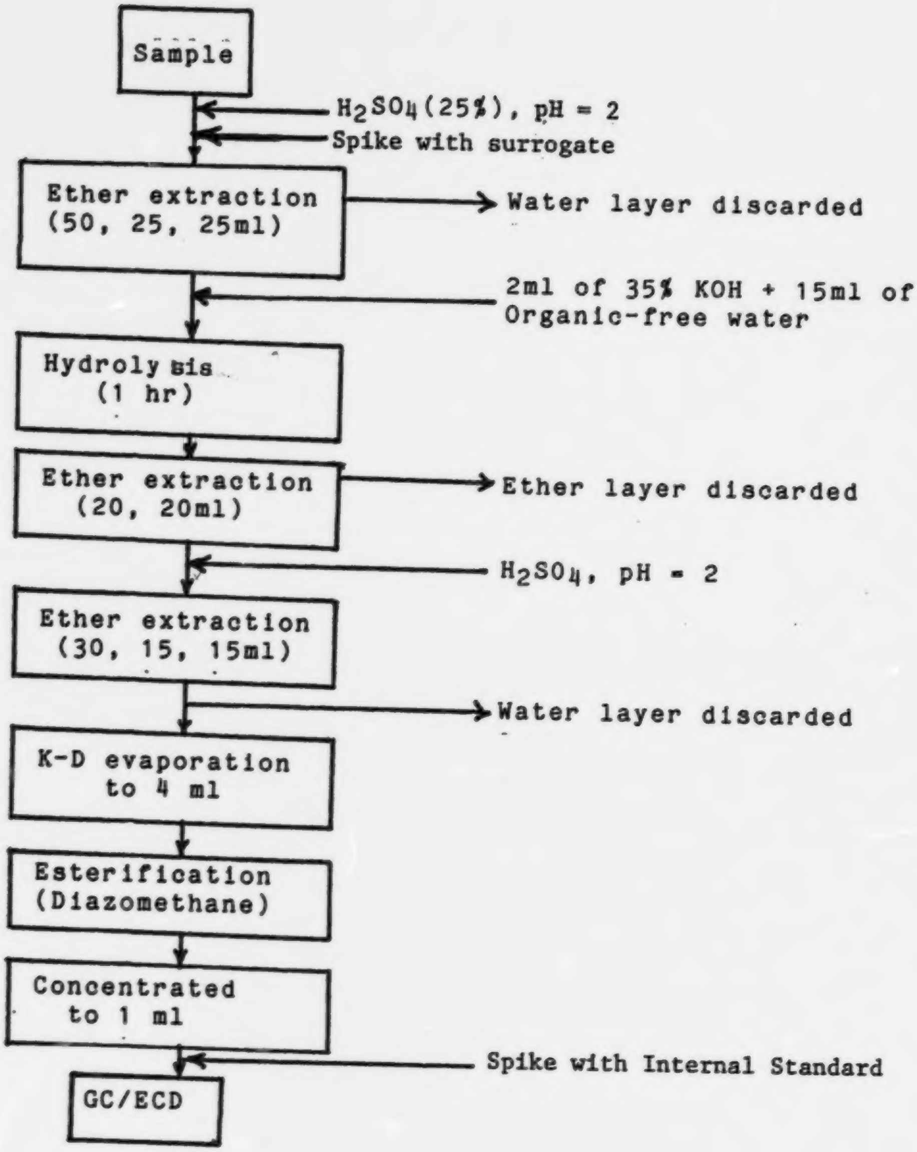


Figure 8 - 2,4-D Analysis Scheme

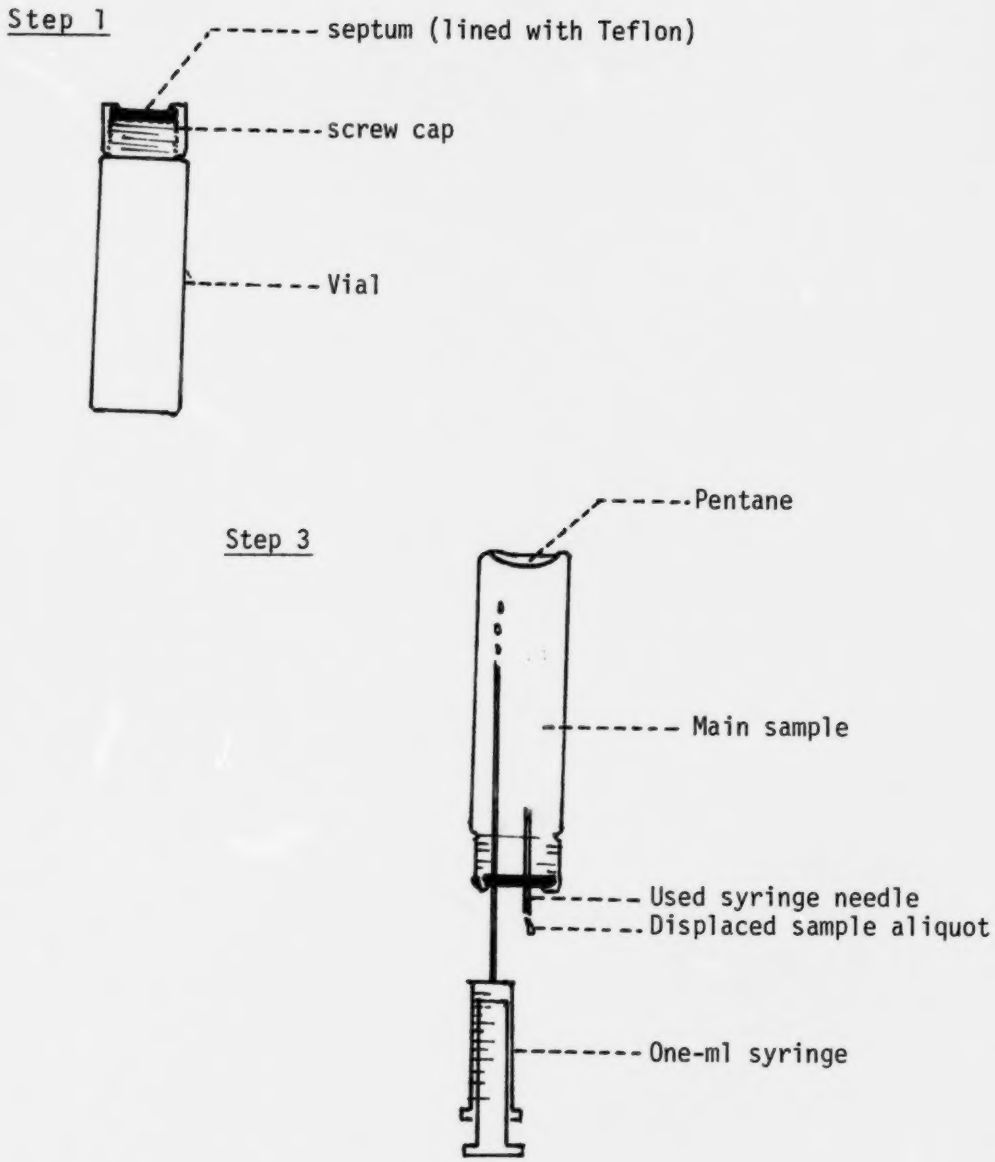


Figure 9. Trichloroethylene Analysis Method

(3) The vial was turned on end and one ml of n-pentane was injected up into the vial through the septum using a one-ml syringe; forcing (displacing) one Ml of sample from the vial via a pre-inserted needle from a used syringe

(4) The vial was reversed (righted) and shaken for 3 minutes.

(5) One microliter of the internal standard, 100 ppb of dichlorobiphenyl (DCBP), was used to spike the pentane layer.

(6) One microliter of the pentane layer by gas chromatography using an electron capture detector.

Analytical Methods - Inorganic Model Compounds

Chromium and lead solutions (supernates) were digested first according to the following procedures:

Five ml of nitric acid (1:1) was added to 50 ml of the supernatant in a 150-ml beaker covered with a glass, heated on an electrical plate at 95°C (below boiling point) and refluxed to near dryness. The solution was cooled, 4 ml of concentrated nitric acid was added and the contents were refluxed to near dryness again. After cooling, 1 ml of 1:1 nitric acid was added, followed by three (3) ml of hydroperoxide (30%). The contents were warmed on the hot plate until effervescence subsided. The beaker was cooled and two increments of 1 ml hydroperoxide was added with warming until the effervescence was minimized and no change in appearance was noted. Another one (1) ml of 1:1 nitric acid was added, followed by refluxing for ten more minutes. The solution then was transferred to a 50-ml volumetric flask and diluted to the mark with distilled water.

A Perkin Elmer Model 703 atomic absorption spectrophotometer with an HGA-2200 graphite furnace was used to analyze the samples.

Conditions for chromium and lead analyses are listed in Table 7.

Table 7 HGA Conditions for Cr and Pb Analyses

		Opt. Dry		Opt. Char.		Opt. Atm.		
Metal	(nm)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Temp (°C)	Time (sec)	Gas Flow (ml/min)
Cr	357.9	105	30	1200	50	2700	10	35
Pb	283.3	105	30	500	30	2300	10	40

Method Validation (QA/QC)

To complement the QA/QC plan for the adsorption studies, method validation studies of the USEPA methods were conducted (Figure 10 outlines the general QA scheme for analytical operations).

The model compounds for method validation ("PP" or priority pollutants) were:

(1) The "six-organic compound mixture" of base/neutral-extractable compounds and acid-extractable compounds, viz.

phenol
aniline
pentachlorophenol
isophorone
naphthalene
bis(2-ethylhexyl phthalate)

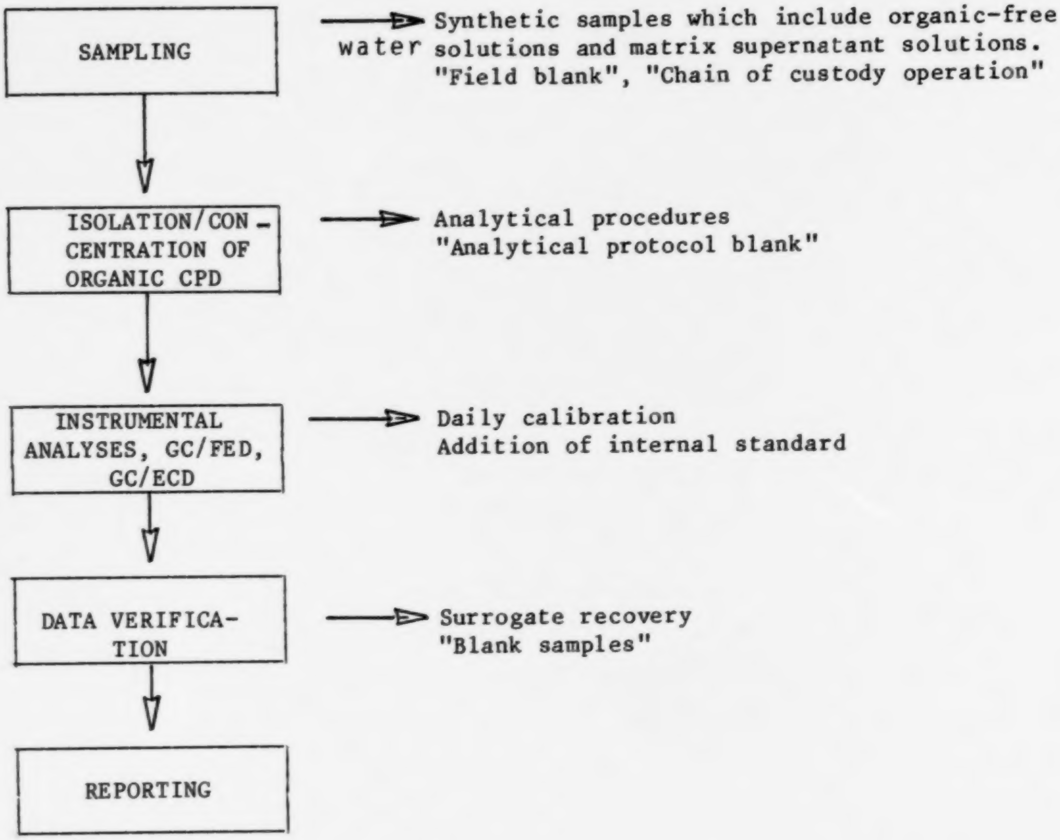

SAMPLING
Synthetic samples which include organic-free water solutions and matrix supernatant solutions.
"Field blank", "Chain of custody operation"
ISOLATION/CONCENTRATION OF ORGANIC CPD
Analytical procedures
"Analytical protocol blank"
INSTRUMENTAL ANALYSES, GC/FED, GC/ECD
Daily calibration
Addition of internal standard
DATA VERIFICATION
Surrogate recovery
"Blank samples"
REPORTING

Figure 10 General QA Scheme for Analytical Operations

(2) trichloroethylene (which is "purgeable")

(3) 2,4-dichlorophenoxyacetic acid ("2,4-D", a pesticide)

(4) A mixture of two heavy metal ions (lead and chromium)

For the method validation studies, three spiking levels (e.g., 150, 500, and 1500 ppb) were used. In addition to the compounds listed above, the following "surrogates" were introduced to the model systems during sample preparation:

di-n-butyl phthalate	(base/neutral extractable surrogate)
2,4-dichlorophenol	(acid-extractable surrogate)
"2,4,5-T"	(pesticide surrogate)
1,1,1-trichloroethane	(purgeable-compound surrogate)

The first two (extractable) surrogates were introduced to the six-component samples, the "2,4,5-T" to the "2,4-D" samples, and trichloroethane to the trichlorethylene series.

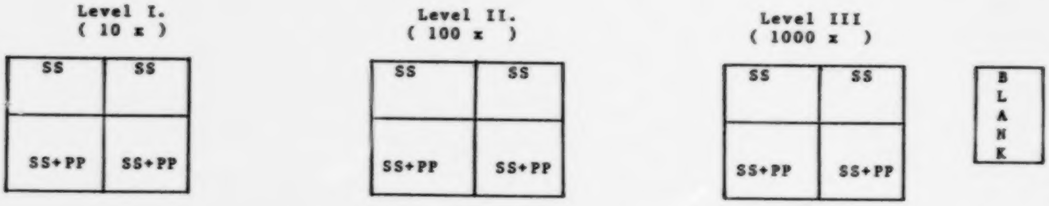
The procedure used for the sample preparation scheme is demonstrated in two steps and by representations in Figure 4.8 whereby the percentage recoveries of all the model compounds (and their associated standard deviations) could be established. (Note: Selection of concentration levels was based on (a) the detection limit of the instrument/detector and (b) the solubility of the compounds of interest).

In the case of the non-matrix study step (no lignin, no adsorption; no interferences), each small rectangle represents one sample consisting of:

(1) a "blank" - simply, organic-free water,
(2) Organic-free water spiked with a combination of

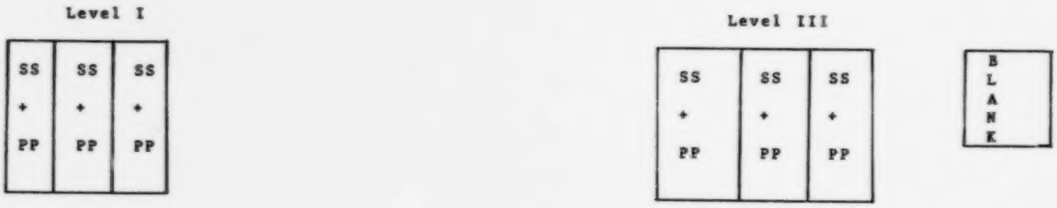
Figure 11 Sample Preparation Scheme for Methods Validation Study

Step 1. 100ml of organic free water spiked with model compounds and selected surrogates at three different concentration levels.



Step 2. Matrix influence study:

100 ml of matrix supernatant spiked with model compounds and surrogates.



(SS = surrogates only; A SS+PP = surrogates and priority pollutants) one of the model compounds (PP = priority pollutant) along with an appropriate surrogate (SS).

(3) Organic-free water spiked with surrogate compounds only

In the case of the study of the influence of the "matrix" (lignin) upon the statistical reliability of the analytical methodology, samples are prepared from organic-free water (100 ml) which has been mixed with 250 mg of pristine lignin in a 125-ml, square-shaped, wide-mouth bottle, agitated in an incubator (Freas 815 Low-temperature Incubator) for four hours at 19°C, and then filtered through a sterilized membrane of 0.45 thickness (Gleman Sciences, Inc.). This supernate is spiked with the model priority pollutants (PP) and/or a corresponding surrogate (SS) - or, if not spiked, it acts as a "blank".

This approach provided internal quality control.

Prior to chromatographic analysis, an internal standard was introduced into the organic concentrates, after the required analytical work-up. The internal standard approach was established to quantify gas chromatographic analysis and to assure the linearity of response of gas chromatographic detectors during the determinations of the pollutants and surrogates. The concentration was calculated based on the response factor (RF), which is defined as follows:

$$RF = \frac{A_p \; C_{IS}}{A_{IS} \; C_p}$$

where A_p = integrated area of pollutant or surrogate peak
A_{IS} = integrated area of internal standard
C_p = amount of pollutant or surrogate in the concentrate
C_{IS} = amount of internal standard in the concentrate

The internal standards for different groups of the organics are listed in Table 8.

Table 8 Internal Standards

Group of Compound	Internal Standard	Concentration in the Concentrate	Instrument
Extractables	Hexamethylbenzene (HMB)	20 ppm	HP 5830 GC capillary column
2,4-D	Dichlorobiphenyl	10 ppm	capillary column
	r-Hexachlorobenzene	500 ppb	Perkin-Elmer Sigma 1 packed column
Trichloro-ethylene	Tetrachloroethylene	100 ppb	capillary column
		200 ppb	Perkin Elmer Sigma 1 packed column

The calibration curves and/or the corresponding statistical reliability data obtained for analyses of each of the eight organic model compounds are presented in the following respective figures and tables.

Trichloroethylene	Fig. 12	Table 9
2, 4-D	Fig. 13	Table 10
Phenol	Fig. 14	Table 11
Aniline	Fig. 15	Table 12
Isophorone	Fig. 16	Table 13
Naphthalene	Fig. 17	Table 14
Pentachlorophenol	Fig. 18	Table 15
Bis(2-ethylhexylphthalate)	Fig. 19	Table 16

A typical chromatogram for the Method Validation study of the six-component model compound solution (aniline, phenol, isophorone, naphthalene, pentachlorophenol, bis(2-ethylhexyl-phthalate), which are representative of base/neutral-extractable compounds and acid-extractable compounds found in hazardous wastes, and the two surrogates (2, 4-dichorophenol and di-n-butylphthalate), and the internal standard (hexamethyl benzene) is presented in Figure 20.

A typical chromatogram for trichloroethylene with its surrogate (trichloroethane) and an internal standard (tetrachloroethylene) is given in Figure 21.

A typical chromatogram for the model compound "2,4-D", its surrogate ("2,4,5-T") and the internal standard, r-hexachlorobenzene, is presented in Figure 22.

The results of the the method validation studies for the mea percent recoveries (p) and standard deviation (S_p) of the organic compounds, by employing the USEPA standard methods, are presented in Table 17. The initial results for trichloroethylene gave a standard deviation (S_p) of 17%, due to the presence of head space in the sample vial in the initial method. The improved analytical method described herein displayed a standard deviation

Table 9. Trichloroethylene Standards

Concentration	Response Area	x Sx	Linear Regression
100 ppb	4.3863	x = 4.7024	
	4.6234	Sx = 0.2678	
	4.7757	(5.69%)	
	5.0243		n = 20
200	9.2303	x = 9.1215	
	8.9804	Sx =	r = 0.9918
	8.8467		
	9.4286		a = 0.6237
300	12.6259	x = 12.8289	
	12.2813	Sx = 1.2279	b = 0.04161
	14.6007	(9.57%)	
	11.8076		
400	16.3766	x = 17.6187	
	17.6804	Sx = 0.8656	
	18.2562	(4.91%)	
	18.1617		
500	20.8443	x = 21.2576	
	22.7053	Sx = 1.0494	
	20.2393	(4.94%)	
	21.2414		

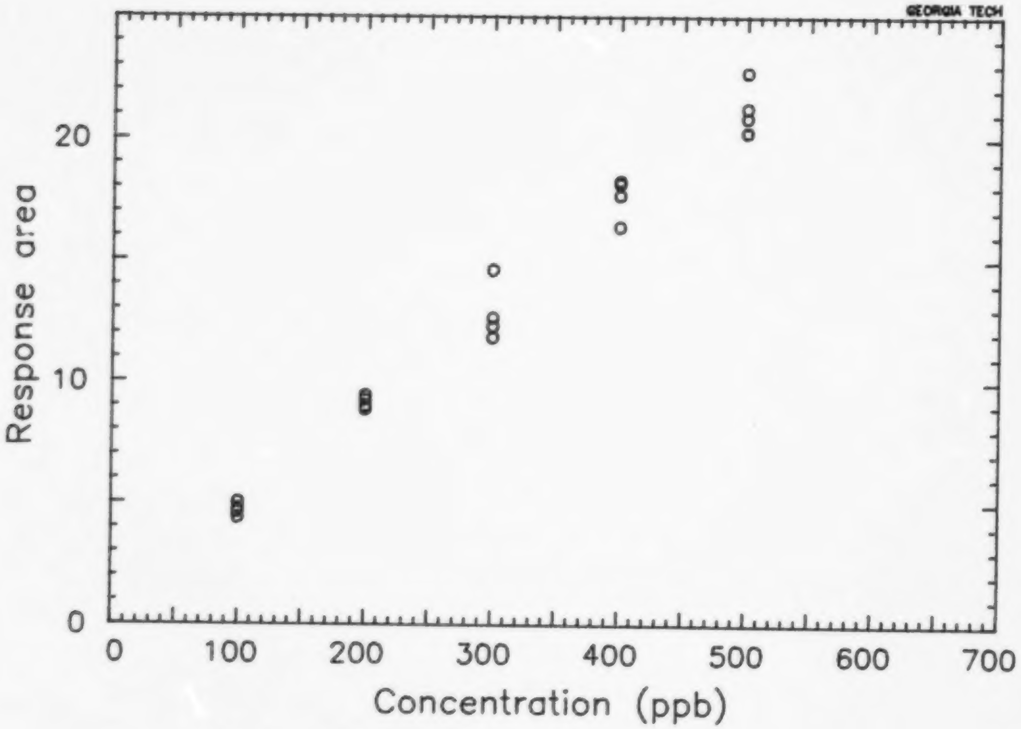


Figure 12 Standard Curve of Trichloroethylene

Table 10. 2,4-D Standards

Concentration	Response Area	x Sx	Linear Regression
1.0 ppm	4.4801	x = 4.2418	
	4.2378	Sx = 0.2757	
	4.3927	(6.5%)	
	4.8566		
2.5 ppm	6.9686	x = 7.3476	
	7.2550	Sx = 0.4876	n = 22
	7.1091	(6.64%)	r = 0.9901
	8.0576		
5.0 ppm	15.1072	x = 16.6245	a = 2.8572
	15.5123	Sx = 1.5685	b = 2.3968
	17.5009	(9.43%)	
	18.3776		
10.0 ppm	26.5702	x = 28.4804	
	30.7300	Sx = 1.7096	
	28.2894	(6.00%)	
	28.3321		
	27.7088		
20.0 ppm	50.6011	x = 49.8769	
	51.3251	Sx = 4.0829	
	54.6457	(8.19%)	
	43.4713		
	49.3414		

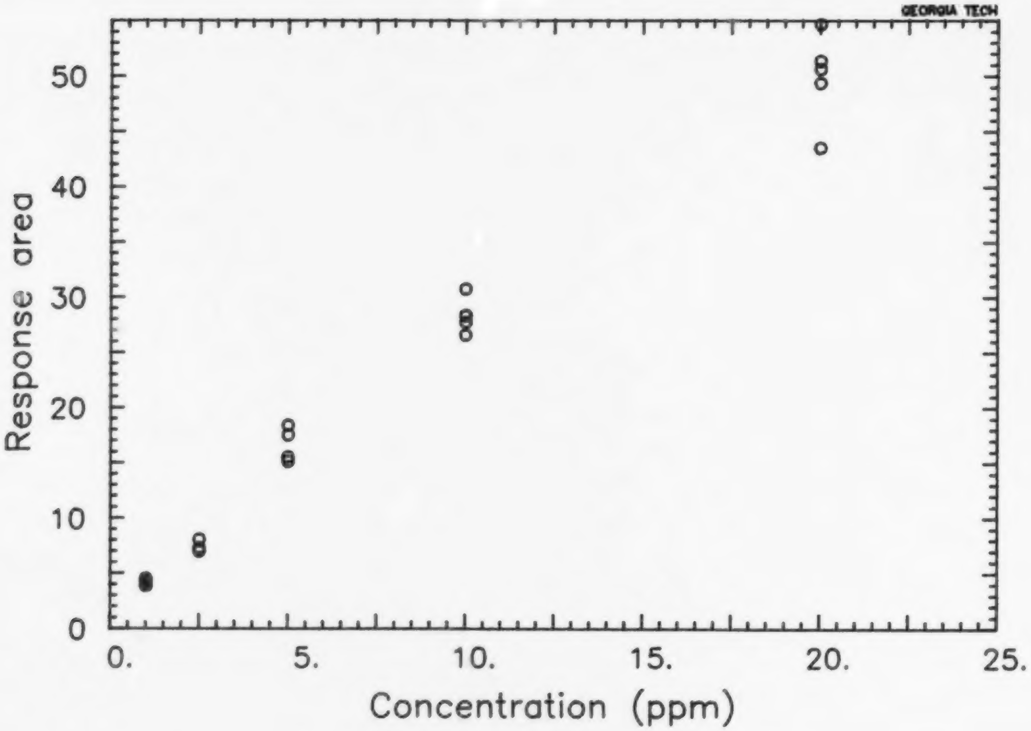


Figure 13 Standard Curve of 2,4 – D

Table 11. Phenol Standards

Concentration	Response Area	x	Sx	Linear Regression
5 ppm	874 1,029 .			
10 ppm	2,047 2,912 2,268 2,517	x = 2436	Sx = 370.89 (15.22%)	5-10 ppm n = 7 r = 0.9604 a = -164 b = 255.9
50 ppm	10,578 21,385 19,911	x = 1729.12	Sx = 5860 (33.89%)	5 or 200 ppm
100 ppm	44,938 43,518 43,731	x = 44,062	Sx = 765.8 (1.74%)	n = 13 r = 0.9682 a = 9490.3 b = 519.6
150 ppm	78,652 71,093 71,135 72,806	x = 73422	Sx = 3577.1 (4.8%)	
200 ppm	52,368 89,395 90,749 60,784	x = 73324	Sx = 1964.9 (26.8%)	

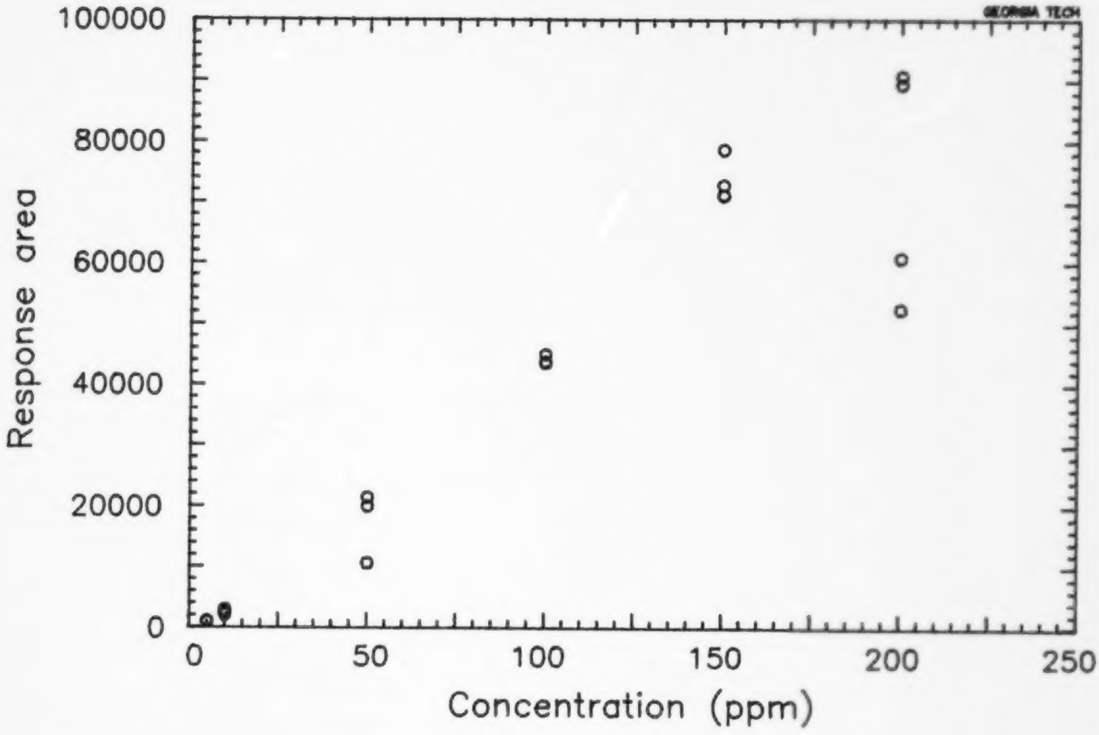


Figure 14 Standard Curve of Phenol

Table 12. Aniline Standards

Concentration	Response Area	x	Sx	Linear Regression
10 ppm	1,144			
	1,330			
50 ppm	21,588	x = 21627	Sx = 803.2 (3.71%)	.50 200 ppm n = 13
	21,922			
	22,450			
	20,547			
100 ppm	44,527	x = 43485	Sx = 1149.1 (2.6%)	r = 0.9981 a = 1440.6 b = 410.3
	44,085			
	43,427			
150 ppm	60,878	x = 61938	Sx = 819.78 (1.32%)	
	62,692			
	62,463			
	61,780			
200 ppm	84,936			

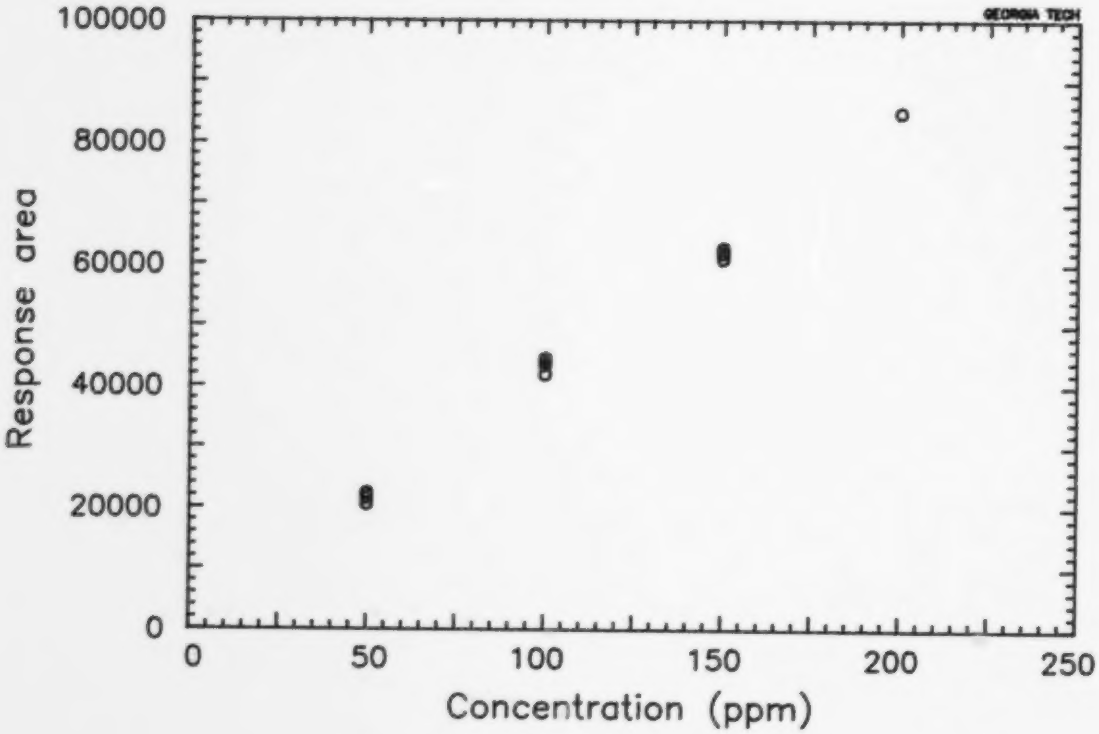


Figure 15 Standard Curve of Aniline

Table 13. Isophorone Standards

Concentration	Response Area	X Sx	Linear Regression
5 ppm	1,687	x = 1670	
	2,271	Sx = 429.7	
	1,371	(25.73%)	n = 21
10 ppm	3,021	x = 2864	r = 0.9992
	2,883	Sx = 137.66	a = 1851.85
	2,883	(4.81%)	b = 443.22
	2,679		
50 ppm	18,609	x = 18857	
	19,563	Sx = 1020.25	
	17,383	(5.94%)	
100 ppm	40,846	x = 41442	
	41,534	Sx = 417.41	
	41,820	(1.01%)	
	41,569		
150 ppm	63,844	x = 64875	
	64,844	Sx = 789.6	
	65,059	(1.22%)	
	65,754		
200ppm	88,523	x = 88,085	
	87,652		

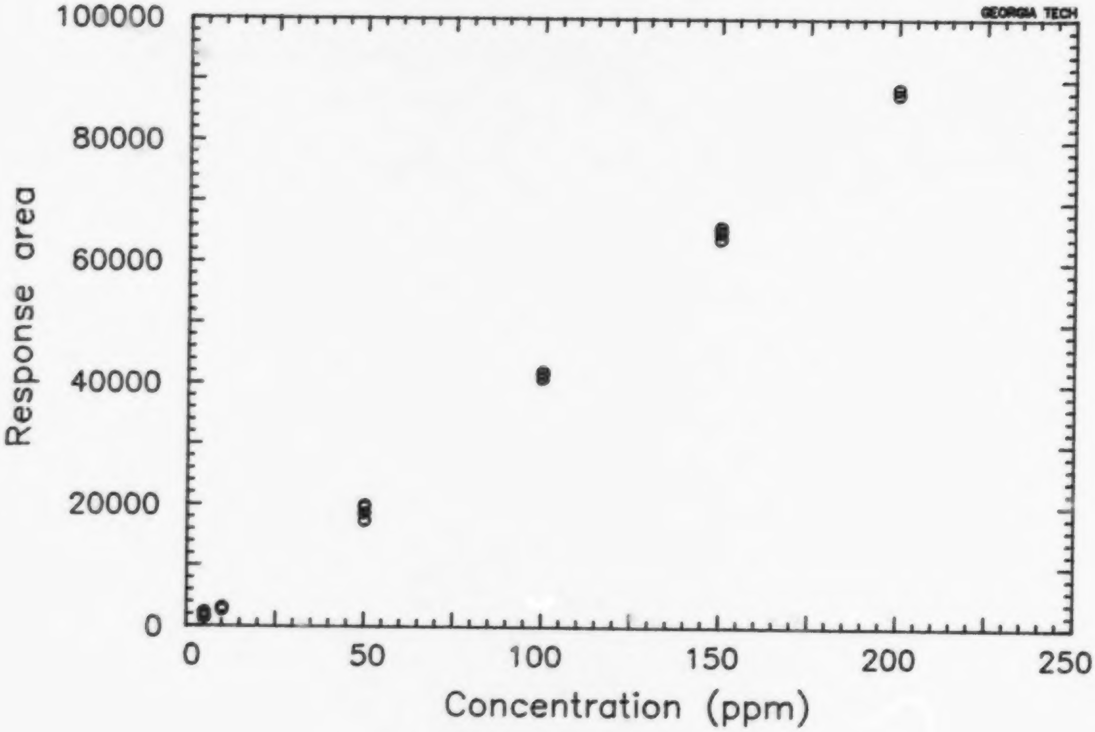


Figure 16 Standard Curve of Isophorone

Table 14. Naphthalene Standards

Concentration	Response Area	x	Sx	Linear Regression
5 ppm	3,032	x = 3609		
	3,679	Sx = 635.07		
	4,480		(17.60%)	5-200 ppm
	3,175			n = 22
10 ppm	6,074	x = 6203		r = 0.9987
	6,131	Sx = 118.08		a = 2409.55
	6,302		(1.90%)	b = 755.24
	6,304			
50 ppm	32,520	x = 33,323		
	33,586	Sx = 609.65		
	33,610		(1.83%)	
	33,950			
100 ppm	68,390	x = 69,859		
	69,737	Sx = 1213		
	71,353		(1.74%)	
	69,954			
150 ppm	108,236	x = 110,776		
	111,114	Sx = 1732		
	111,933		(1.56%)	
	111,822			
200 ppm	150,983	x = 152,845		
	154,707			

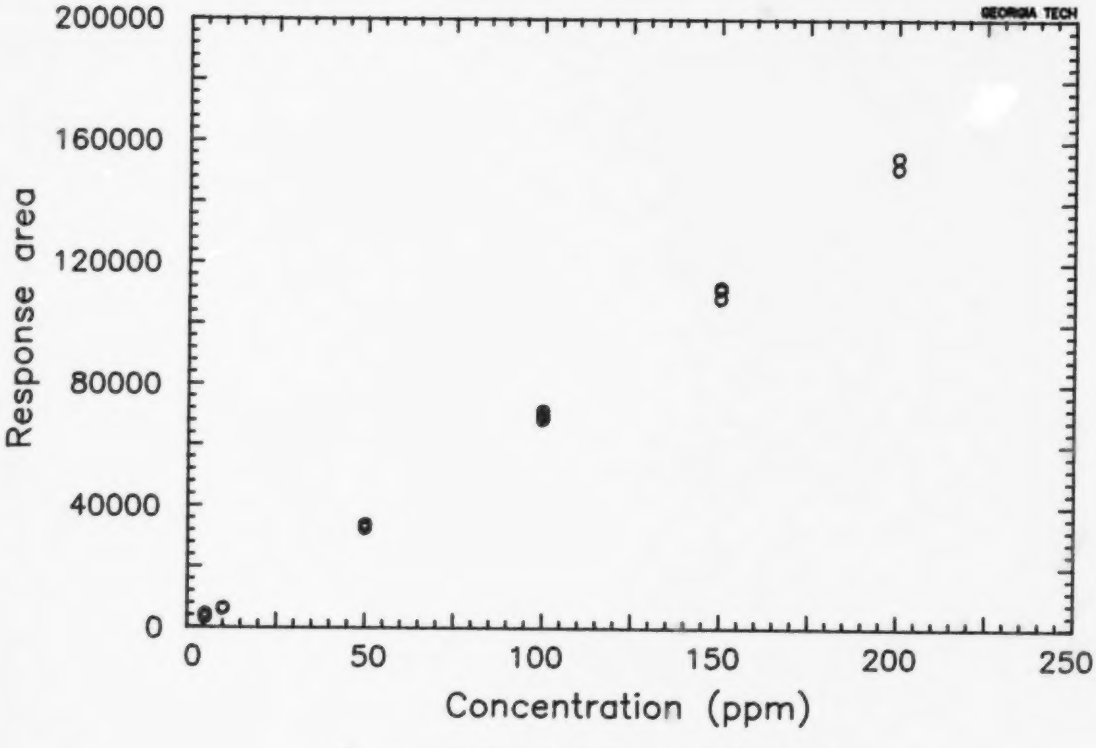


Figure 17 Standard Curve of Naphthalene

Table 15. Pentachlorophenol Standards

Concentration	Response Area	x	Sx	Linear Regression
50 ppm	671 600 713	x = 661.3	Sx = 57.12 (8.64%)	5-200 ppm
100 ppm	2,921 2,268 2,697 3,252	x = 2784	Sx = 412.96 (14.83%)	n = 13 r = 0.9879 a =-1643.75 b = 45.49
150 ppm	4,880 5,226 5,699 5,611	x = 5354	Sx = 376.89 (7.04%)	
200 ppm	7,804 6,804	x = 7304		

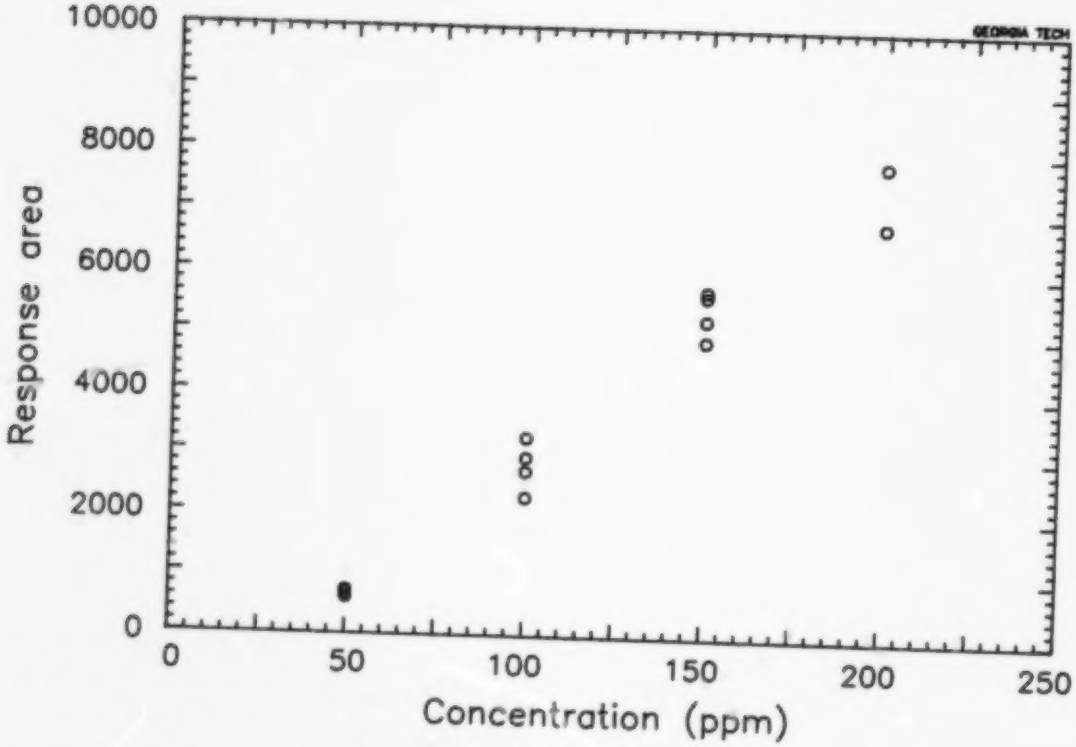


Figure 18 Standard Curve of Pentachlorophenol

Table 16. Bis (2-ethylhexyl) phthalate

Concentration	Response Area	x Sx	Linear Regression
5 ppm	772 574 754	x = 700 Sx = 109.49 (15.64%)	5-150 ppm n = 18 r = 0.9525 a = 82.86 b =151.99
10 ppm	1,717 1,553 1,466 1,520	x = 1564 Sx = 108.18 (6.91%)	
50 ppm	8,051 9.477 8,110	x = 7727 Sx = 1857 (24.03%)	
100 ppm	13,135 11,078 19,756 19,210	x = 15795 Sx = 4347 (27.52%)	
150 ppm	18,873 17,505 27,715	x = 22495 Sx = 5059 (22.49%)	
200 ppm	27,901 28,166	x = 28.034	

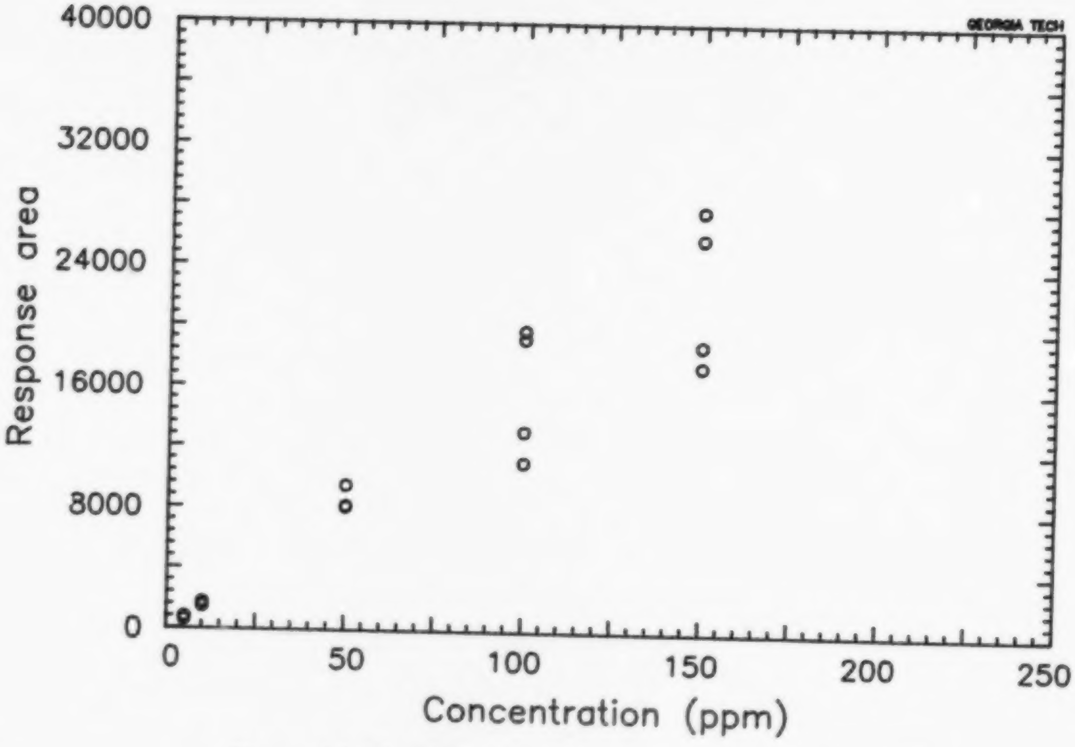
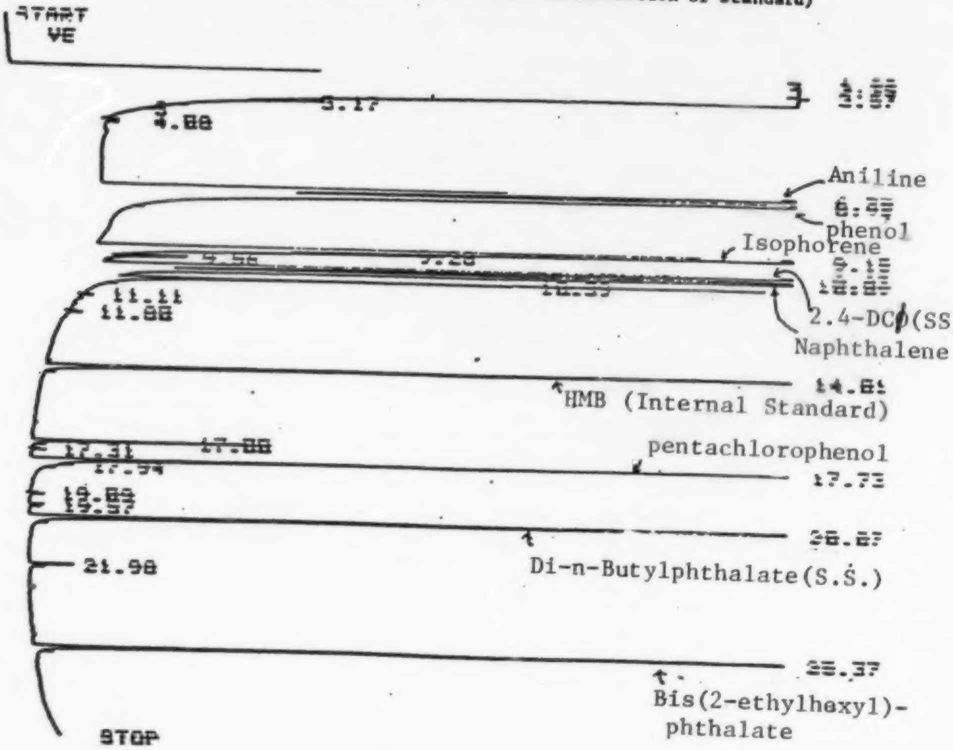


Figure 19 Standard Curve of bis (2-ethylhexyl)phthalate

Figure 20.

Chromatogram of base/neutral and acid extractable compounds (shows one concentration of standard)



Surrogates: 2,4-Dichlorophenol , Di-n-Butylphthalate

Internal standard : HMB

Column 90B, length: 13 m , Column pressure: 0.35 kg/cm^2
Temp.1 40, time1 4, temp.2 290, time2 10
Detector : FID

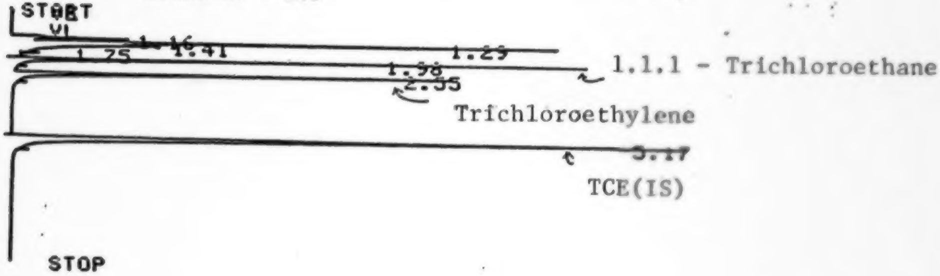
Figure 21.

Chromatogram of trichloroethylene and 1,1,1-trichloroethane

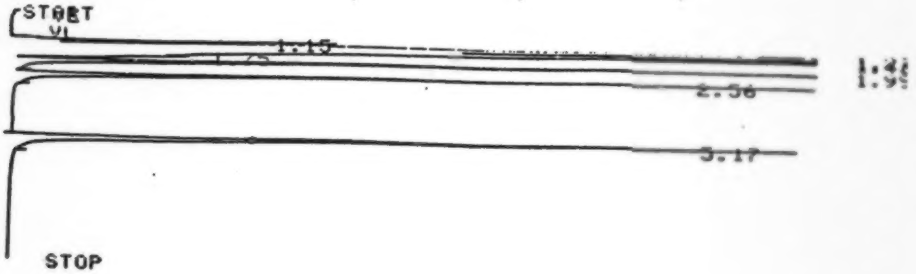
(Tetrachloroethylene as the internal standard)

(1,1,1-trichloroethane as the surrogate)

Column: OV101, length 15 m
Column pressure : 0.3 kg/cm^2
Temp.1 40, time1 10, temp.2 250, time2 5.
Detector : ECD



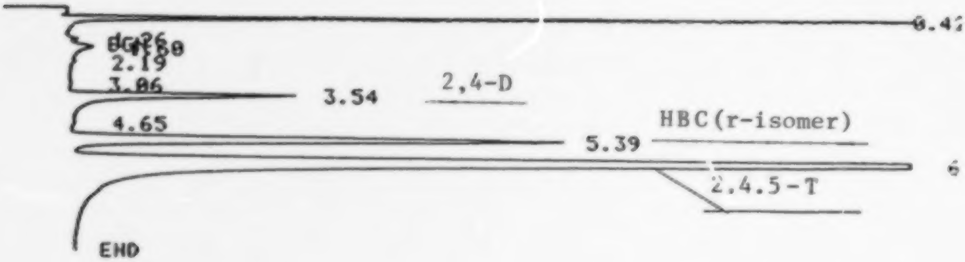
```
hp 5830A
 RTIME          AREA     AR%
  1.16          12680    4.83
  1.29          47220   17.97
  1.41          22960    8.74
  1.75           2947    1.12
  1.98          37650   14.33
  2.55          40840   15.54
  5.17          98500   37.48
```



```
hp 5830A
 RTIME          AREA     AR%
  1.15          25980    1.99
  1.27         709200   54.22
  1.43         251400   19.22
  1.75          23650    1.81
  1.99         113000    8.64
  2.56          76740    5.87
  5.17         108000    8.26
```

Figure 22.

Chromatogram of 2,4-D, Surrogate and Internal Standard



Surrogate: 2,4,5-T **Internal Standard:** HBC (r-isomer)

Column: 1.5% OV17, 1.95% QFI on 100/200 Chromosorb WHP
Length: 6 ft. Internal diameter: 2 mm
Initial oven temp., 180°C
Initial time, 15
Detector temp., 250°C

(Sp) of only 7.1% as shown in Table 17 for the surrogate.

The corresponding results for method validation studies of chromium and lead in deionized water are given in Table 19.

The precision had been established to be within the critical range (RC) + three (3) standard deviation (S_x) and the accuracy of analyses to be within + 30% of the mean percent recovery (P). Using these criteria, the recoveries of surrogates of all samples at every experimental stage were calculated to validate the analytical methods.

Kinetics Studies

The principal objective of the kinetic studies was to determine the maximum time required for adsorption equilibrium to be achieved using the large particle size (30/40 mesh) pristine lignin and to estimate the adsorption capacity.

The kinetics studies as originally planned were overly ambitious given time, manpower, and funding availability. Nevertheless, the principal objective was largely accomplished due to the behavior of the lignin isolate which had to be run under acidic pH conditions since partial solubilization of the isolate was experienced at neutrality (pH=7) and in slightly basic medium (pH=9). Consequently, all runs were made at pH = 3.5 ± 0.5 and this resulted in the elimination of some planned experiments. Furthermore by standardizing on one particle size range initially we were able to complete a comprehensive screening of the model compounds with the available lignin. Plans for "size selection" studies were deferred until later in the project and, since the isotherm equilibrium studies would require an extensive battery of analyses, it was planned to

Table 17 **RECOVERY AND STANDARD DEVIATIONS FOR ORGANIC COMPOUNDS**

COMPOUND	Mean % Recovery and S.D. in Organic-Free Water	Mean % Recovery (p) Std. Std. Dev. (Sp) Matrix
Aniline	90.3 ± 15.65	67.0 ± 18.5
Phenol	69.3 ± 8.3	79.4 ± 15.7
Isophorone	82.7 ± 11.6	69.1 ± 15.93
Naphtalene	58.3 ± 4.14	54.5 ± 17.26
Bis-(2-ethylhexyl)phthalate	143.3 ± 9.29	
Pentachlorophenol	73.4 ± 5.57	
2,4-D	91 ± 33.75	70 ± 20.8
2,4-Dichlorophenol*	73.98 ± 17.15	
Di-n-butylphthalate*	94.37 ± 30	
2,4,5-T*	88.17 ± 30.0	

* Surrogates

Table 18 **Recovery of Trichloroethane (surrogate)**

For Organic-Free Water:

Spiking Concentration (ppb)	Conc. found (ppb)	Mean Recovery ($\bar{P}$) (%)
200	174.2	87.1
	193.4	96.7
	184.7	92.4
	202.7	101.4
	172.9	86.5
	206.5	103.3

$\bar{P}$ = 94.6% S_p = 7.1

For Matrix Study:

200	144.8	72.4
	178.0	89
	148.8	74.4
	181.8	90.9

$\bar{P}$ = 81.7 S_p = 9.6

Table 19

RECOVERY AND STANDARD DEVIATIONS OF INORGANIC MODEL COMPOUNDS

Compound	Mean % Recovery ($\bar{p}$) and S.D. in Deionized-Water
Chromium	9.49 + 0.32
Lead	1.73 + 1.06

perform such analyses when it was established that high values of adsorption capacity could be achieved with one or more physical or chemical modifications of the pristine lignin isolates.

Procedure

As shown in Table 20 a total of four sets of analyses were conducted:

(1) A solution of all organic compounds (excepting 2,4-D)
(2) A solution of 2,4-D
(3) A lead salt solution (standard commercially available)
(4) A chromium salt solution (standard commercially available)

Each analytical set of test compounds consisted of nine duplicate sample bottles (a total of eighteen samples). The first two sample bottles were designated as "controls" and 0.25 g. of lignin. The remaining sixteen sample bottles of each set were filled with organic-free water which was spiked with specific initial concentrations of model compounds. To fourteen of each set's bottles, a charge of 0.25 g of 30/40 mesh lignin was added and the time of charging was recorded with time monitored thereafter. The remaining two bottles of each set were charged with 0.75 g of 30/40 mesh lignin and times were also recorded. All sample bottles were placed in an incubator at 19°C, agitated on a rotor, and allowed to equilibrate for specified periods in the incubator.

Samples (duplicate) were removed from the incubator at intervals of increasing length (e.g., 1 hour, 2 hour, 4 hour, etc.) as shown in Table 20 and were worked up for analyses of specific model compounds per established procedures. In the

Table 20 Experimental Matrix of Duplicate Analysis for Adsorption Kinetics Study

Group	Control	1 hr	2 hr	4 hr	8 hr	1 day	4 day	4 day*
7-org. mix.	2	2	2	2	2	2	2	2
2, 4-D	2	2	2	2	2	2	2	2
Lead	2	2	2	2	2	2	2	2
Chromium	2	2	2	2	2	2	2	2

* Bottles contained 0.75g of lignin. All other contain 0.25 of lignin.

studies a laboratory centrifuge was used to separate the solid lignin from the supernatant liquid by revolving at 2000 RPM for thirty (30) minutes (This time was not included as part of the "equilibrium time"). All centrifuge tubes were capped to minimize contamination and loss of volatile model compounds, e.g., trichloroethylene. The supernates were analyzed according to the procedures outlined in the previous section of this report.

Materials and Apparatus

(a) The lignin was the ethanolic isolate, PH-047, which was screened to a particle size range of 30/40 mesh. Some discoloration of the organic-free aqueous solutions occurred on addition of this lignin. However, there was apparently little or no interference with the chromatographic analyses.

(b) Samples bottles were 125-ml capacity wide-mouth square shaped botles fitted with Teflon-level screw caps

(c) Incubator-rotor

(d) pH = 4

(e) Temperature = 19°C

Size Study: Effect on Adsorptive Capacity

Based on the kinetics studies for the adsorptive capacity of organic and inorganic compounds by pristine lignin a size study was conducted for the purpose of studying surface area influence on the adsorptive capacity. Different size fraction/ranges i.e. 30/40, 40/60, and 60/100 mesh of ethanol-extracted lignin and sodium hydroxide-extracted lignin (60/100 only), were investigated.

Method and Materials

Three sizes of ethanol-extracted lignin and one size of NaOH-extracted lignin were used. For each size,duplicate sample bottles dosed with 0.25 g of lignin in 100 ml of aqueous solutions of the model compounds (120 ml for trichloroethylene) were agitated in a rotating mixer for 4 days at 19°C. The samples were then centrifuged to separate the lignin and supernatant per procedures described earlier (Section 4). The scheme of this study is shown in Table 21.

Table 21 Scheme of Size Study

LIGNIN	CONTROL	7-MIXTURE	2,4-D	Pb	Cr
Ethanol-extracted					
30/40		2	2	2	2
40/60		2	2	2	2
60/100	2 X 4	2	2	2	2
NaOH-extracted					
60/100	2 X 4	2	2	2	2

The final (residual) concentrations of the model compounds in the supernate, after equilibration for four days, were analyzed using the same analytical techniques as previously described for the kinetic studies.

Activated Carbon Adsorption Isotherm Study for Model Compounds

In this study data for adsorption isotherms of activated carbon for the various model compounds (of extractable organics, purgeable organics, pesticides and heavy metals) were generated experimentally (Part I. Complete isotherm experiments) or were collected from the research literature and, in this latter case, a single point determination and verification of the adsorption isotherm reported for that model compound was replicated in the laboratory (Part II Replication of adsorption isotherm data in the literature).

A. Material

Adsorbent: Calgon Filtrasorb 400, 30x40 mesh

Adsorbate: 2,4-D, Aniline, Chromium, Phenol, Pentachlorophenol, Isophorone, Bis(2-ethylhexyl)phthalate, Naphthalene, and Trichloroethylene.

Solution: Aqueous solution

B. Scheme for Isotherm Studies with Activated Carbon

The whole study involved two parts. For those compounds, for which there is no isotherm data in the USEPA source the activated carbon adsorption isotherms were generated completedly (Part I). The scheme is shown in Table 22. For other compounds where USEPA data existed one point for each of the reported isotherms was checked in duplicate to verify and compare the experimental result with the EPA data base. This scheme (Part II) is listed in Table 23.

Table 22 Complete Isotherm Study

Compound	C_o	Carbon dose (mg/100 ml)							
2,4-D	2.5 ppm	1	2.5	5	10	20	30	40	50
Aniline	10 ppm	1.25	2.5	5	10	25	50	100	200
Chromium	10 ppm	5	12.5	25	50	100	150	200	250

Table 23 Scheme for Single Point Check of Adsorption Isotherms in EPA data base

Compound	C_o(ppm)	Carbon dose (mg/100 ml)
Phenol	10	20
Pentachlorophenol	10	6.25
Naphthalene	8	6.25
Bis(2-ethylhexyl)-phthalate	20	3.0
Isophorone	1.25	2.5
Trichloroethylene	1	12

Adsorption Capacity Study of Steam-Exploded Wood

A sample of steam-exploded Tulip poplar was screened through a +10 mesh screen and prepared for screening of its adsorption capacity using adsorbent doses of 50 mg and 500 mg in 100 ml of solution of the model compounds, with the exception that a 120 ml volume was used for trichloroethylene determinations. All experimental conditions (pH, temperature, equilibrium time, initial concentration of adsorbates) were the same as those employed in the adsorption studies of lignin.

Adsorption Isotherm Study: Pristine Lignin

The adsorption capacity of five individual model compounds on a selected sample of an alkaline-isolated lignin was determined according to the scheme outlined outlined in Table 24. The materials and conditions were as follows:

Adsorbent: NaOH-extracted lignin 60x100; Source: steam-exploded Tulip poplar
Adsorbate: Phenol, naphthalene, "2,4-D",trichloroethylene, and chromium
Solution: Aqueous
PH: 3.5 ± 0.5
Temp: 23 ± 2°C

Table 24 Scheme for Lignin Adsorption Isotherm Study

Compound	Co (ppm)	Lignin dose (milligrams in 100ml)							
Phenol	10	10	25	50	100	200	300	400	500
Naphthalene	8	10	25	50	100	200	300	400	500
Trichloro-ethylene	2	5	10	25	50	100	150	200	250
2,4-D	2.5	1	2.5	5	10	20	30	40	50
Chromium	10	5	10	25	50	100	150	200	250

Note: 1. All samples were duplicated including the blanks (not shown).

Section 5 RESULTS AND DISCUSSION

ISOLATION OF PRISTINE LIGNIN FROM STEAM-EXPLODED WOOD

Yields and Material Balances

The steam-exploded wood which was studied extensively in this project was prepared by the hydrothermal decompression of the hardwood chips of Tulip poplar (L. tulipifera) at 350 psig and for a residence time of four minutes. Initial separation processing of this steam-exploded wood centered on the extraction of the lignin component in "pristine form", by use of 95% ethanol and Soxhlet extraction, after having first hot water-washed the steam-exploded wood to remove any residual organic compounds arising during the hydrothermal treatment process, in particular the hydrolysis products of the hemicellulose fraction. "Pristine" lignin was isolated by precipitation in a mildly acidic solution, filtration, and drying. The yields and mass balances for these isolates are summarized in the section entitled "Ethanolic Isolater - Tulip Poplar".

The same feedstock was treated with 0.1N sodium hydroxide, following the water-washed elimination of hydrolysis products, in a single-stage batch extraction. Results for the yields and mass balances for these extractions are presented in the section entitled "Alkaline Isolates - Tulip Poplar".

A rather extensive series of alkaline extractions was run on a second supply of steam-exploded wood which was produced by Stake Technology Ltd. (Canada) using the hardwood Aspen (Populus tremuloides). This hardwood was reportedly processed with steam at 315 psig for (4) minutes.

The sample was not considered to be typical of Stake processed aspen but was supplied to Georgia Tech to assist in larger scale lignin isolation work. However, the supply of GIT-produced steam-exploded Tulip poplar proved to be adequate for the project and only limited investigation was conducted on the lignin isolated from the Stake-produced steam-exploded aspen. The results of yield and mass balance calculations are presented in the section entitled "Alkaline Isolates - Aspen".

The yields and mass balances for individual experiments were calculated as follows:

Let Wi = initial mass of dry steam-exploded wood (corrected for moisture content), in grams
Wf = final mass of dry steam-exploded wood after complete extraction (corrected for moisture content), in grams
TWL = Wi-Wf = total sample mass loss (total weight loss), in grams
L = total mass of dry lignin isolated (recovered) (corrected for moisture content), in grams

MB = mass balance, in grams
= FEL - FLR
FEL = Fraction of lignin extracted (%)
= TWL/Wi x 100

FLR = Fraction of lignin recovered (%)
= L/Wi x 100
= "Yield"

In an ideal experiment, the mass balance (MB) should equal zero, i.e. FLR = FEL.

A comparison of the values of the mass balance (MB) with the total weight loss in the sample (TWL) is a measure of the experimental losses (or efficiency) of the isolation procedure.

Ethanolic Isolates - Tulip Poplar

Nine isolation experiments were conducted using 95% ethanol as the extractant. The yields and mass balances of these experiments are summarized in Table 25.

The poor material balances in some experiments, most notably PH048, may be attributable to variability in the efficiency of the pre-water wash step (removal of adsorbed, residual hydrolysis products from hydrothermal treatment), since the repeatability of the yields of ethanolic isolates (avg. 7.5%) is excellent, indicating efficient isolation of lignin.

Alkaline Isolates - Tulip Poplar

Nineteen alkaline extractions were conducted with the GIT-prepared steam-exploded Tulip poplar (NaOH1-NaOH19). The extractions were conducted in a single-step because of the efficiency of extraction (Figure 23). The results of yield and mass balance calculations are presented in Table 26. The average recovery (yield) was 31.9% (Range: 26.2-39.4%). The recovery represents a 4.25-fold increase over that achieved with ethanol.

According to Fieber (8), steam-exploded Tulip poplar which was processed at 350 psig for three (3) and five (5) minutes had an extraction yield of 31.3% and 40.4% with ethanol and 38.6% and 50.0% with 0.1N NaOH, respectively. Since the material used in this study came from the same source, there is a suggestion of post-reactivity (condensation and crosslinking?) which significantly affects ethanol solubility but has a more modest effect on alkaline extraction. (The material had been stored for four years in a plastic-lined steel drum in an environmentally-controlled building.)

Table 25   Yields and Mass Balances - Ethanolic

BATCH	Wi	MB	TWL	FEL	FLR	L grams
SH038A	316.5	-0.24	18.36	5.8%	5.9%	18.6
SH038B	291.0	- 5.2	23.28	8.0%	9.8%	28.5
PH040	301.2	0.1	21.40	7.1%	7.1%	21.5
PH041	362.8	19.8	46.6	12.8	7.2%	26.1
PH042-43	622.7	2.68	47.54	7.64	7.2%	44.9
PH045	904.3	22.93	84.73	9.4%	6.8%	61.8
PH046	916.9	32.84	104.04	11.3%	7.8%	71.2
PH047	909.3	19.28	89.78	9.9%	7.8%	70.5
PH048	922.8	54.0	122.7	13.3	7.5%	68.8%

Wi = DRY SAMPLE WEIGHT (Grams)
MB = MASS BALANCE (Grams), FEL-FLR
TWL = TOTAL WEIGHT LOSS (Grams), Wi-Wf
FEL = FRACTION EXTRACTED LIGNIN, TWL/Wi x 100
FLR = FRACTION LIGNIN RECOVERED, L/Wi x 100
L = LIGNIN ISOLATED, (Grams)

Table 26 Yields and Mass Balances - Alkaline Isolates (Tulip Poplar)

BATCH	Wi	MB	TWL	FEL	FLR	L
NaOH1	219.8	20.9	78.4	35.0	26.2	57.5
NaOH2	218.8	12.0	80.4	36.7	31.3	68.4
NaOH3	218.3	13.9	75.95	34.8	28.5	62.1
NaOH4	218.6	10.1	72.94	33.4	28.7	62.8
NaOH5	218.3		75.25			64.2
NaOH6	218.4	14.9	78.94	34.5	29.4	64.0
NaOH7	218.4	7.6	78.64	36.0	32.5	71.0
NaOH8	219.2	6.3	73.6	33.6	30.7	67.3
NaOH9	219.4	9.8	76.7	34.9	30.5	66.9
NaOH10	219.5	7.9	66.8	30.4	34.0	74.7
NaOH11	219.0	13.9	72.33	33.0	39.4	86.2
NaOH12	218.5	8.9	71.44	32.7	28.7	62.8
NaOH13	218.8	9.4	80.6	36.8	32.5	71.2
NaOH14	220.9	17.7	84.9	38.4	30.6	67.5
NaOH15	218.3	7.0	78.3	35.8	32.6	71.3
NaOH16	219.6	9.0	72.7	34.4	30.3	75.3
NaOH17	219.2	2.6	63.4	33.1	34.3	73.9
NaOH18	219.2	-10.5	63.4	28.9	33.7	73.9
NaOH19	219.7	-51.3	35.4	16.1	39.4	86.7

Key: See Table 25

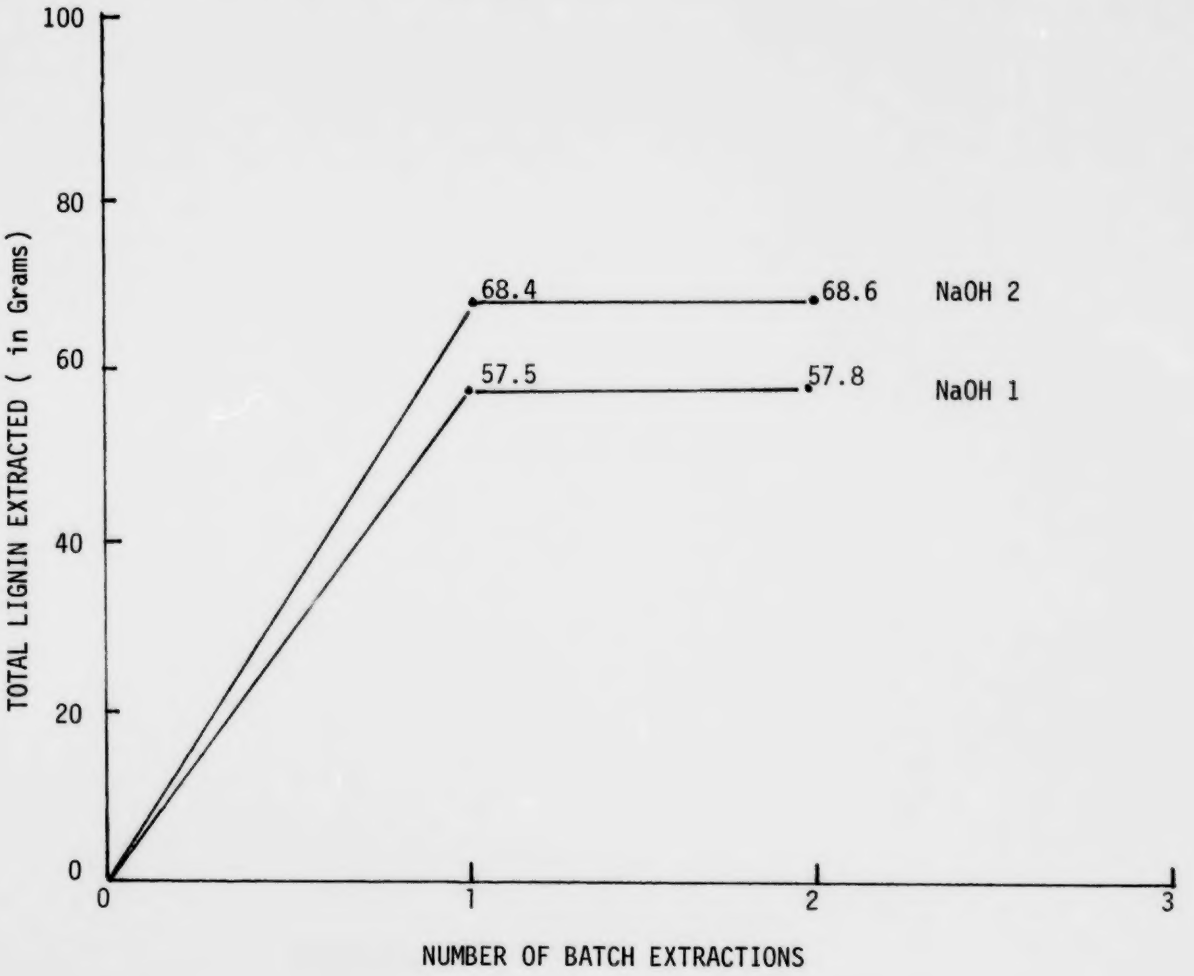


FIG. 23 ALKALINE EXTRACTION EFFICIENCY

Table 27 Yields and Mass Balances - Alkaline Isolates (Aspen)

Batch	Wi	MB	TWL	FEL	FLR	L
PSL1	224.2	53.6	97.1	43.4	30.3	43.2
PSL2	22.8	45.9	89.1	40.1	34.3	43.2
PSL3	223.1	39.2	89.6	40.1	22.6	50.4
PSL4	224.1	40.3	90.5	40.4	22.4	50.2
PSL5	223.8	39.4	90.4	40.4	22.8	51.0
PSL6	223.6	42.2	91.6	41.0	22.1	49.4
PSL7	223.5	33.7	89.8	40.2	25.1	56.1
PSL8	224.2	35.1	90.3	40.2	24.6	55.2
PSL9	223.4	27.4	82.9	37.1	25.1	56.0
PSL10	222.4	31.1	82.1	36.9	22.9	51.0
PSL11	225.8	34.8	85.9	38.5	22.9	51.1
PSL12	225.9	23.6	79.0	35.3	24.8	55.4
PSL13	225.9	18.0	79.3	35.5	27.4	61.3
PSL14	226.1	26.2	81.8	36.6	24.9	55.6
PSL15	226.0	9.1	65.6	29.3	25.3	56.5
PSL16	226.0	42.2	89.3	39.9	21.1	47.1
PSL17	225.6	14.2	49.1	35.4	29.1	64.9
PSL18	225.3	13.3	82.6	37.1	31.1	69.3
PSL19	225.7	34.9	89.4	40.0	24.4	54.5
PSL20	226.5	34.7	88.2	39.3	23.9	53.5
PSL21	226.2	28.3	84.1	37.6	25.0	56.0
PSL22	226.2	14.2	79.9	35.7	29.3	65.7
PSL23	226.5	36.8	91.0	40.6	24.2	54.2
PSL24	226.3	37.3	92.8	41.4	24.8	55.5
PSL25	226.3	32.4	85.4	38.1	23.7	53.0
PSL26	226.0	19.7	85.3	38.1	29.3	65.6
PSL27	226.3	38.6	91.3	40.8	23.5	52.7
PSL28	225.3	36.0	91.3	38.3	22.2	49.4
PSL29	225.8	35.2	90.0	40.0	24.5	54.8
PSL30	225.3	34.0	85.5	38.3	23.1	51.5
PSL31	225.6	31.0	86.8	38.9	25.0	55.8
PSL32	226.2	36.6	84.6	37.8	21.4	48.0
PSL33	226.3	41.0	94.0	42.0	23.7	53.0

Key: See Table 25

Alkaline Isolates - Aspen

The results of extraction with alkali using the Stake-processed steam-exploded aspen hardwood are presented in Table 27. The average (n = 33) % recovery (yield) of lignin was 25.8% for the aspen (vs. 31.9% for Tulip poplar) via the alkaline process. There is a generally consistent mass balance which suggests that about one-third of the material extracted from the steam-exploded wood is being lost during work-up evidently as solubles in the filtrate and washings. It was found, during the functional group analysis (acid-base titrations), that lignin isolates would not dissolve in neutral or acidic media unless they were first dissolved in alkali and then were slowly neutralized or acidified. Presumably there is an increase in the hydrodynamic volume of the lignin macromolecule, opening up the structure to more facile solvation.

Solubility Behavior: Potential Extraction Procedures

While delignification (pulping) of wood chips by different solvents has been investigated over the years, there existed no comprehensive study of the delignification of steam-exploded wood. Both ethanol (95%) and alkaline (0.1N NaOH) have advantages and disadvantages - as expressed, for example, by the molecular weight distribution and percentage recovery of their lignin isolates. The organic solvent (ethanol) provided a clean, light powder as a product with a surface area of $30m^2/g$ while the alkaline lignin was a dark, friable and hard solid with a very low surface area ($0.1\text{-}0.3m^2/g$). Because of the desirability of developing an isolation process in the future which would overcome many of the deficiencies of the ethanolic and alkaline isolation (e.g., filterability and pumpability), a study of the solubility behavior of steam-exploded wood was undertaken in order, ultimately, to identify alternative solvent/non-solvent systems for the extraction and isolation of pristine lignin products.

The solubility behavior of an ethanolic lignin isolate (PH-040) in various organic solvents, per ASTM-D3132, is presented in Table 28. Surprisingly, ethanol proved to be a poor solvent near room temperature (without agitation) despite having been used originally to isolate the lignin. Dimethylformamide (DMF), which is an extremely polar solvent, was decidely the best solvent based on the observed rate of solubilization. The results of assessing the same ethanolic lignin isolate (PH-040) with (a) agitation/shaking and (b) heat (52°C), for fifteen (15) minutes is given in Table 29. Some significant improvement in the rate of solubilization was noted with several solvents on agitation although little improvement was noted with the increase in temperature from ambient temperature to 52°C (water bath).

The resolubilization of both ethanolic - and alkaline-lignin isolates in 95% ethanol, 0.1NaOH and their solubility in water was examined, the results of which are reported in Table 30. All samples were soluble completely in the alkali while all ethanolic-lignin isolates were nearly "completely" soluble in ethanol. A small portion of these isolates could not be solubilized at room temperature suggesting that these might be accounted for by higher molecular weight fractions. As part of this assessment, PH048 ethanolic lignin isolate was placed in deionized water for the 24-hour period and a slight solubility was noted from the discoloration of the water although the bulk of the solid appeared undistrubed as a brown powder on the bottom of the test tube. Somewhat similarly, the two alkaline-lignin isolates gave a faint gold discoloration when placed in water for 24-hours. In later adsorption studies, no such effects were

Table 28 Solubility of a Lignin Isolate (PH-040) per ASTM-D3132 Method

Solvent	Solubility 24 hours	 7 days
hexane	I	I
ethyl ether	I	I
cyclohexane	I	I
n-butyl acetate	B	C*
40% cyclohexane/60% toluene	I	I
toluene	I	I
50% toluene/50% dioxane	B	C*
methylene chloride	B	C*
dioxane	B	C
carbon disulfide	I	I
n-butanol	B	C*
acetanilide	B	C*
dimethyl formamide	C	C
ethanol	B	C*
methanol	B	C*
ethylene glycol	B	C

Key:
I = insoluble
B = barely soluble
C = completely soluble
C*= partially (or incompletely) soluble

Table 29 Solubility of Lignin Isolate (PH-040) with (a) Shaking and (b) at 52°C for Fifteen (15) Minutes

Solvent	With Shaking	Followed by Heating at 52°C for Fifteen (15) Minutes
hexane	I	I
ethyl ether	I	I
cyclohexane	I	I
n-butyl acetate	B	B
40% cyclohexane/60% toluene	I	I
toluene	I	I
50% toluene/50% dioxane	B	B
methylene chloride	B-C*	B-C*
dioxane	C	C
carbon disulfide	I	I
n-butanol	B	B
acetanilide	B-C*	B-C*
dimethylformamide	C	C
ethanol	B-C*	B-C*
methanol	B-C*	B-C*
ethylene glycol	C	C

Table 30 Solubility of Lignin Isolates in Aqueous Sodium Hydroxide, 95% Ethanol and Water Per ASTM-D3132

	0.1N NaOH	95% Ethanol	H_2O
PH040	C	C*	
PH041	C	C*	
PH042, 43	C	C*	
PH045	C	C*	
PH046	C	C*	
PH047	C	C*	
PH048	C	C*	B
NaOH1	C	B	I
NaOH2	C	B	I

Key:

C = completely soluble
C*= highly soluble (minor amount undissolved)
B = barely soluble (light gold discoloration)
I = insoluble (trace gold discoloration)

noted with the alkaline lignin isolate but discoloration of aqueous solutions of model compounds with the ethanolic lignin isolates was noted. A total organic carbon (TOC) analysis of an originally organic-free water in which both isolates were dispersed and then separated (to isolate the supernates) showed no carbon in the alkaline isolates supernate but 25ppm TOC was found in the ethanolic isolate's supernate, which corresponded to a 1.6% solubility in water.

The solubility behavior of lignin isolate (PH-040) is represented by the plot of the hydrogen bonding index of solvents vs. the corresponding solubility parameter of the solvents and its solubility range of lignin while complete insolubility is expressed in Figure 24. The shaded area represents the solubility range of lignin while complete insolubility is indicated external to this area. Thus, by appropriate selection of lignin-solvent and non-solvent pairs, and by correlation of material solubility of these pairs, identification of optimal systems for efficient isolation of lignin may be facilitated.

CHEMICAL AND PHYSICAL CHARACTERIZATION OF PRISTINE LIGNIN

General Background on Delignification

Lignocellulosic materials potentially represent the largest renewable source of chemicals and liquid fuels in the world today. The carbohydrate fraction can readily be converted into sugars and alcohols, while the lignin fraction represents the largest single natural source of aromatic compounds, and could also be used in selected polymeric systems as extenders. Wood has been the primary source of lignocellulosic material consumed by industry, predominantly for the production of cellulose-based pulps. As a result, separation technology involving wood has

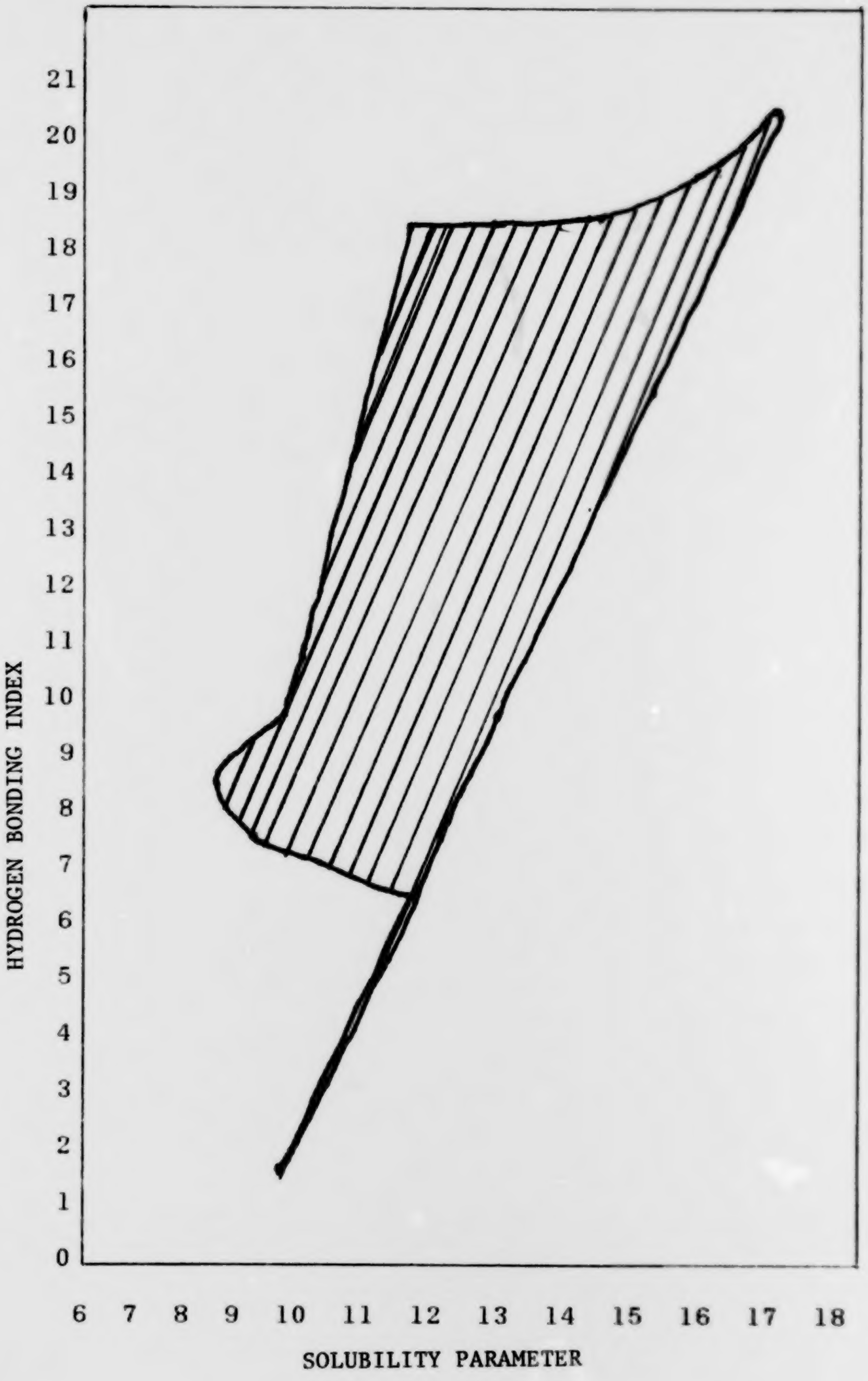


FIG. 24 LIGNIN SOLUBILITY BEHAVIOR

been developed by the paper industry, with its primary objective to produce a high quality cellulose pulp as economically as possible. Three of the major chemical methods developed and currently in use today are the (1) kraft or sulfate, (2) acid sulfite and (3) neutral sulfite processes. These processes employ sulfur-based compounds and acidic or basic pulping liquors which excessively modify the lignin and degrade the hemicelluloses in the wood.

The primary objective of this study was to investigate the relatively "pristine lignin" isolated via the GIT Lignocellulose-to-Ethanol Process and its application as a material for hazardous waste treatment.

The delignification reactions of the primary commercial processes have been modeled experimentally and extensively by reacting known compounds at similar conditions and by determining the products. Based on these studies delignification reaction mechanisms have been proposed. Differences in the delignification mechanisms are clearly a direct result of reaction condition variables for each process, e.g., pH, temperature, nature of the nucleophilic reactant species, etc.. Since this study could not accommodate an investigation of the reaction mechanisms, effect of operational parameters, kinetics, etc. involved in steam-explosion/delignification, one can only infer the comparability of the nature and composition of the "pristine lignin" isolates with those obtained by the primary commercial (pulping) processes.

Chemical pulping processes, it should be emphasized, focus on the isolation of cellulosic fibers (with minimal degradation) by removal of lignin and the hemicellulosic carbohydrate fractions of wood. There are two major types of wood, softwood and hardwood. Softwoods are generally coniferous or evergreen and hardwoods are deciduous or broad-leaved trees. Softwood fibers, or tracheids, are 3-4mm long and hardwood fibers are 0.7-2mm in length. Consequently, pulping operations focus on softwood processing because the longer fibers provide a better pulp for papermaking. The movement towards using lignocellulosic materials as a source of energy and chemical products, to a large extent, focuses on the use of hardwoods since they are not a direct competitive resource for the high-value pulp and paper industry. Moreover, hardwoods tend not to be extensively harvested, except in limited volumes, for example, for furniture production. Consequently, annual growth/production rates of hardwoods exceed their harvesting rates. The growth rates decline because of overcrowding and thinning is not undertaken without commercial outlets. Hardwoods, therefore, provide an attractive raw material on the basis of availability and a concommitant bonus in improving effective regeneration.

Hardwoods provide an additional chemical advantage in that the type of lignin which is associated with hardwoods is different and more easily separable from the other components in wood, than is the lignin associated with softwoods where that lignin is highly and tightly associated with the carbohydrate components even after severe steam-explosion treatment.

The cross section is a typical tracheid cell, which is the water conducting cell of the wood tissue, as shown in Figure 25 (1). The outside layer of a cell is very thin and is called the primary wall, P. Immediately below the primary wall are the three layers of the secondary wall. The middle layer, S_2, is the thickest and has a high cellulose content. The center of the cell is called the lumen. Its size varies from cell to cell, and softwoods generally have larger lumens than hardwoods. Between

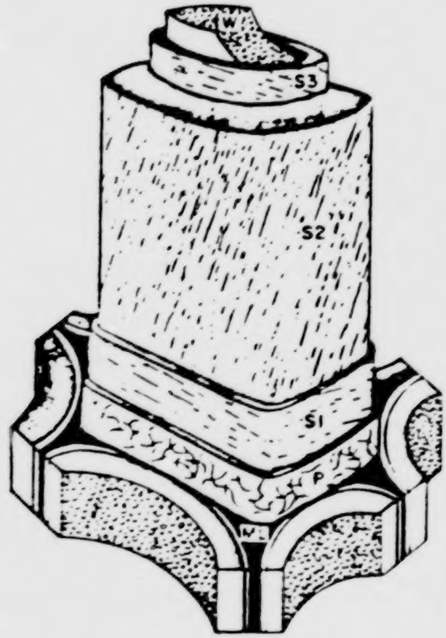


FIG. 25 STRUCTURE OF A TYPICAL TRACHEID CELL IN WOOD (1)

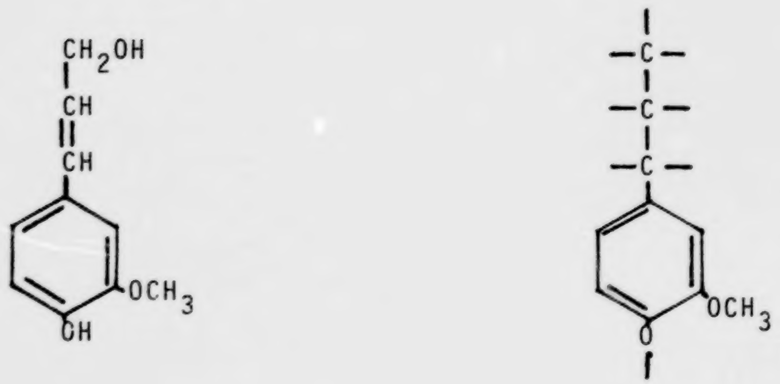
each cell is the middle lamella, ML, a region containing primarily lignin and hemicellulose.

Pulping conditions are designated to minimize cellulose degradation, while maximizing lignin removal. Typically, in conventional chemical pulping processes, reaction temperatures range from 150° to 190°C, reaction times from 1 to 6 hours and pH ranges from 1 to 14. Thus, a wide variety of cellulose pulps are produced with varying purity and quality. The major cellulose degradation reactions occur in acid sulfite pulping and alkaline or kraft pulping. Neutral sulfite pulping is a semichemical process which has little or no cellulose losses.

Aselme Payen, a French chemist and botanist, made the first serious attempt to determine the chemical composition of wood in 1838 (2). He treated wood with nitric acid and strong alkali and then with ethanol and ethyl ether. He was left with a material that resisted these reagents and solvents which he called cellulose.

Payen also realized that he was removing another substance from wood during his isolation of cellulose. This material had a higher percentage of carbon than did the cellulose and it appeared that the cellulose was surrounded or impregnated with this material. Payen called this material lignin.

In Sweden, around 1890, Peter Klason performed the first extensive investigation of lignin chemistry (3). Klason developed the first quantitative method for lignin determination by the application of sulfuric acid. Klason was also the first to suggest that the parent structure of lignin might be a phenylpropane derivative of the coniferyl type (Figure 26).



(I) (II)

Figure 26 Coniferyl Alcohol (I) and Phenylpropane Derivative of the Coniferyl Type (II)

Even though it has been over one hundred years since the discovery of lignin, knowledge of its chemical structure is still incomplete. A chemical structural formula for lignin still cannot be written. Lignin is usually separated from other wood constituents by the application of strong chemical reagents which usually modify the lignin. As a result, the chemical composition of lignin isolated by different preparations often differ extensively.

Lignin cannot be thought of as one individually defined compound. It is really a collective term for a series of structurally related large molecules (Figure 27) (4). This definition can be further refined by including some of the structural properties of lignin; composed of phenyl propane units, contains most of the methoxyl content in wood, is readily oxidized, is soluble in hot alkali and bisulfite, and readily condenses with phenols and thio compounds. Lignin can also be further defined by its formation of aldehydes when treated with nitrobenzene and alkali at elevated temperatures. When softwood lignins are oxidized by nitrobenzene they yield vanillin; hardwoods yield syringaldehyde and vanillin (Figure 28).

The lignin content of wood ranges between 17 and 33%. This value not only varies with species, but also with the age and type of wood being examined. Lignin formation begins when the surface growth of the cell wall has ceased. Initial deposition takes place on the primary wall at the cell corners (Figure 25). Lignification then extends to the intercellular spaces, middle lamella and then into the second wall where the lignin is deposited around the cellullose microfibrils (3).

Fergus et al (5) used ultraviolet microscopy to determine the concentrations of lignin in black spruce (Figure 29). The secondary wall, middle lamella and cell corners contained 22.5%, 49.7% and 84.8% lignin, respectively. Assuming the secondary wall occupies 87.4% of the total volume of the tracheid tissue, it was estimated that the secondary wall contains 72.1% of the total lignin within the tracheid structure. Softwood is composed of two types of cells, tracheid and ray cells, with tracheid cells representing 90-95% of the wood volume.

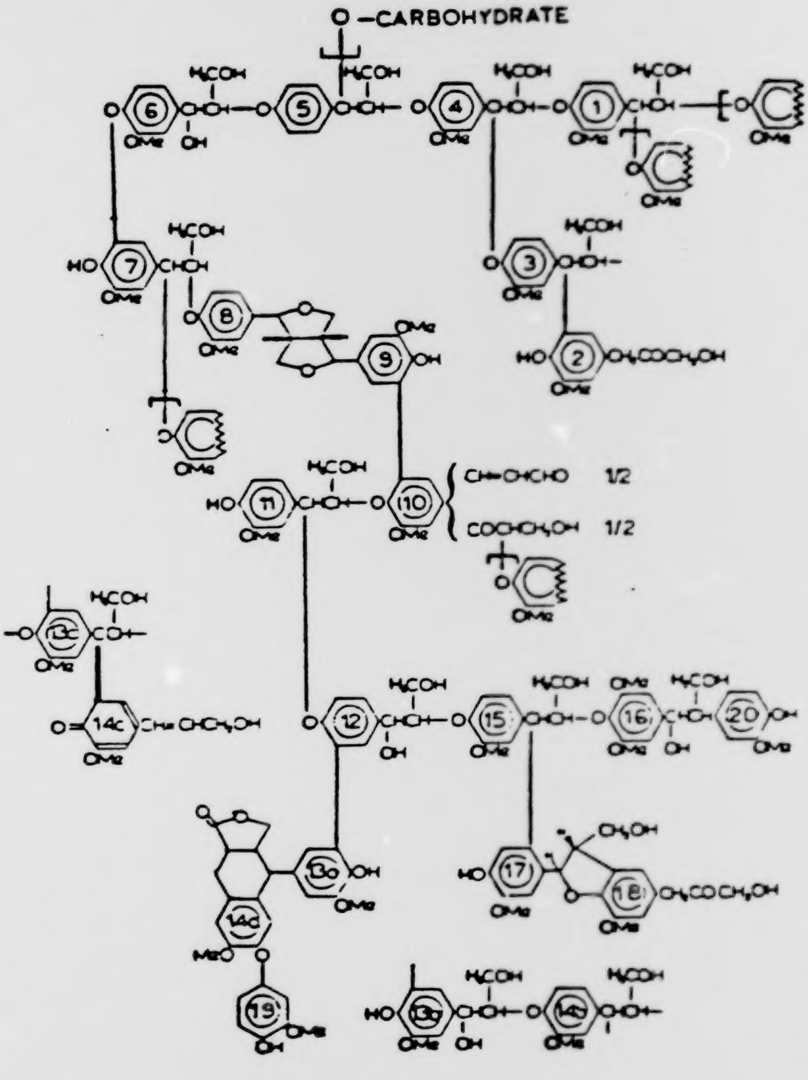
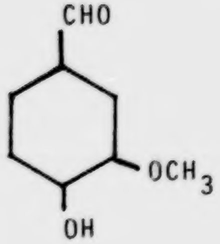
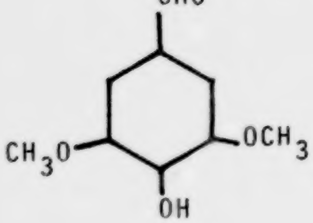


FIG. 27 MODEL CHEMICAL STRUCTURE OF SPRUCE WOOD LIGNIN

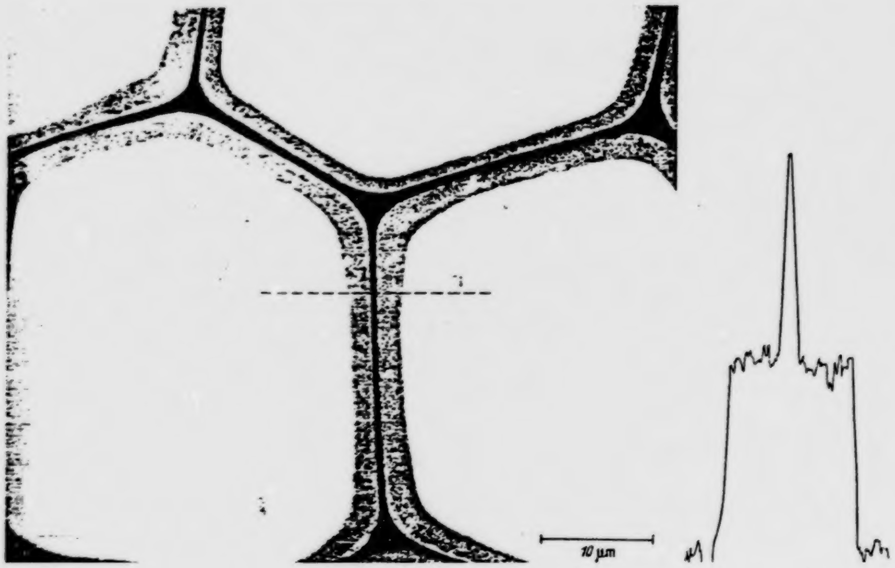


(I)



(II)

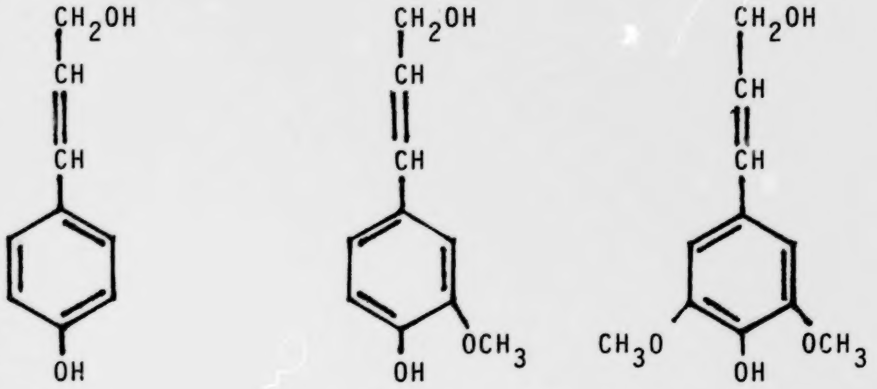
Figure 28 Structures of Vanillin (I) and Syringaldehyde (II)



Notes: (1) UV light @ 240 nm
(2) Densitometer trace across tracheid wall on dotted line.

FIG. 29 CROSS-SECTION OF SPRUCE TRACHEID (5)

It is now known that lignin is an arylpropane based polymer formed from a mixture of three p-hydroxycinnamyl alcohols via an enzyme initiated dehydrogenative polymerization. The precursor molecules are transformed into phenoxy radicals by an electron transfer reaction and oxidative coupling to form the polymeric lignin molecule. The sequence of monomer coupling and the bonds linking these together are probably random. The relative percentage of each of these precursor molecules from which lignin is formed depends on the tree species.



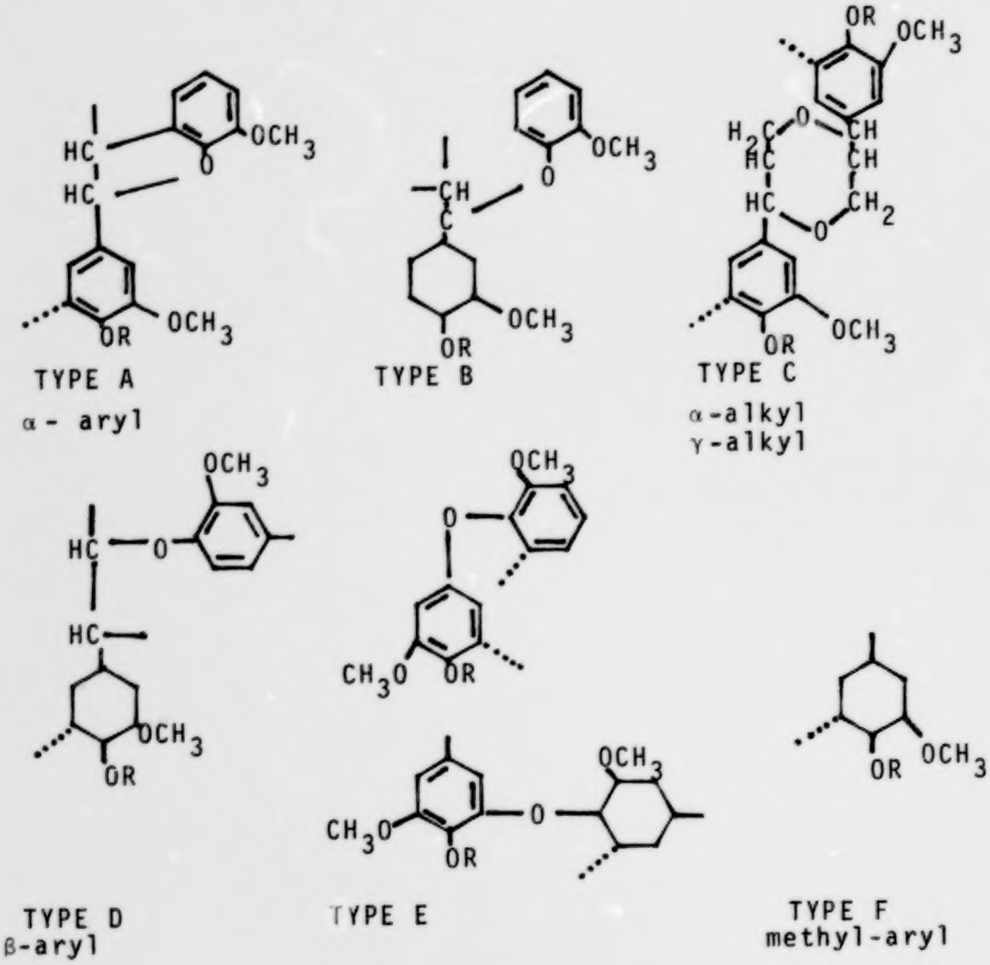
p-Coumaryl alcohol

Coniferyl alcohol

Sinapyl alcohol

p-hydroxycinnamyl alcohols (lignin precursors)

Two-thirds to three-fourths of the arylpropane units in lignin are linked to adjacent units by at least one and, in most cases, two ether bonds. The remaining units are coupled by carbon-carbon bonds. The main types of ether bonds found in lignin are shown in Figure 30. Of these, the beta-aryl (type D) and the methyl-aryl (type F) linkages predominate.



TYPE A
α - aryl

TYPE B

TYPE C
α-alkyl
γ-alkyl

TYPE D
β-aryl

TYPE E

TYPE F
methyl-aryl

Figure 30 Ether Linkages in Lignin

During wood pulping both the methyl-aryl and carbon-carbon bonds are stable. Lignin fragmentation results when beta-aryl and to a lesser extent, alpha-aryl bonds (type B) are cleaved (Figure 30). Cleavage of type A alpha-aryl bonds and type C alpha-alkyl and gamma-alkyl bonds (Figure 30) do not cause fragmentation due to the remaining carbon-carbon bond, but it does increase the hydrophilic nature of the lignin which enhances the subsequent dissolution process. A detailed review of the main reactions involving these ether bonds at different pulping, conditions has been written by Gierer (7). This review is based on studies performed with model compounds containing one or more of the ether groups in Figure 30. Since wood is a heterogeneous material containing three major constituents, all of which react simultaneously during wood pulping, the results from these model compound studies suggest how the corresponding ether groups in the lignin probably react under similar conditions. Until studies are performed which not only include lignin model compounds, but also carbohydrate degradation products, absolute confirmation of the proposed reaction mechanisms does not exist.

The steam-explosion process is not a pulping process since the cellulose fibers are severely degraded (see, e.g., the electron micrographic results in this study). It may however, be viewed as an autohydrolysis chemical reaction with similarities to reaction mechanisms experienced in acid/neutral pulping processes. After loading the wood chips into a pressure chamber under high-pressure steam conditions for a short period of time, explosion of the wood chips is accomplished by the sudden release of pressure. During exposure of the wood to the high-pressure steam, acetic acid and other acids are formed that catalyze the decomposition of hemicelluloses (in particular) and cellulose, cleave p-ether linkages of lignin and chemically modify lignin and carbohydrates. Under ideal conditions, hemicellulose is extensively removed as volatile degradation compounds or readily by aqueous extraction of its residual hydrolyzates, leaving a residue containing lignin, which is neither highly condensed nor extensively associated with carbohydrate components (as is the case in its natural state) but which is readily extractable and separable from the residual cellulose component (the latter material then being in a preferential state for acid or enzymatic conversion to fermentable sugars). The compositional changes associated with steam treatment of Tulip poplar, under conditions employed for the subject of this study, is shown in Table 31 (8). The apparent lignin content increases in steam-exploded wood while the hemicellulose in the wood (pentosan, xylan and arabinan) decreases.

Generalizations for Delignification Reactions (9)

Delignification is defined as the removal of lignin from wood via cleavage of reactive interunit bonds and to a minor extent, the introduction of polar groups into the lignin sructure resulting in an increase in the solubility of the lignin in aqueous solutions. The process of delignification can be summarized in four steps: fragmentation of the polymeric lignin, dissolution of the fragments, diffusion of the dissolved lignin from the wood structure, and condensation of the lignin fragments. The rates of these reaction steps vary and are strongly dependent on the processing conditions.

Fragmentation is the desired reaction during pulping and is accomplished under a wide variety of conditions in industry and the laboratory. The primary reaction variables are pH, temperature, reaction time, concentration of the pulping chemicals and the wood species. In spite of the variety of conditions, the reactions responsible for lignin fragmentation

Table 31 Composition of Untreated Tulip Poplar and Steam Hydrolyzed Wood Product (8)

Units grams/100 grams of Original Wood

	Untreated Tulip Poplar Chips	Steam Hydrolyzed Wood (350 psig, 4 minute)
Carbohydrates		
Glucan	49.7	48.7
Xylan	17.2	1.5
Mannan	3.7	0.8
Arabinan	0.7	0.1
Galactan	1.0	0.2
Soluble Sugars		
Glucose	--	1.1
Xylose	--	5.7
Mannose	--	1.1
Arabinose	--	0.1
Galactose	--	0.7
Lignin	26.7	35.9
Ash	0.4	0.4
Volatiles		
Methanol	--	0.3
Furfural	--	1.6
Acetic Acid	--	2.1

can be generalized in terms of common mechanistic features. Two types of reactions occur during pulping, nucleophilic and electrophilic additions and displacements. The initial reaction is usually nucleophilic. Sites of electrophilic and nucleophilic attack are carbon atoms with high and low electron densities, respectively. By elimination (cleavage) of an alpha or in conjugated structures a gamma substituent, the arylalkane unit forms a quinone methide intermediate. This reaction occurs with phenolic units over the whole pH range, but phenol ethers can only form these intermediates in acidic solutions. The formation of a quinone methide intermediate involves the loss of two electrons and produces low electron density sites at the carbonyl atom and at the carbon atoms in vinylogous positions to the carbonyl atom (12). Enols from alpha-carbonyl follow analogous transitions.

Almost all lignin units and most initial degradation products contain p-hydroxy or alkoxy arylpropane groups. The electron orbitals of the oxygen atoms in these groups overlap with the bond orbitals of the aromatic ring, creating high electron density sites ortho and para to the oxygen. Also, lignin units containing a conjugated aliphatic double bond attached to the aromatic ring have a high electron density at the beta-carbon. These sites of high electron density are attacked by electrophiles during wood pulping. Condensation, the undesired reaction which occurs during delignification, is a generalized term used to describe a class of reactions involving the quinone methide intermediates and their addition of nucelophiles to convert back to an aromatic structure. The nucleophile can either be a species formed during lignin fragmentation or an externally supplied species, such as hydroxide, hydrosulfide, hydrosulfite or sulfite ions. The lignin-lignin condensation reactions result in a decrease in reactivity, and solubility, and an increase in the molecular weight of the lignin byproduct. Condensation reactions involving external nucleophiles primarily reduce reactivity and improve solubility of the lignin byproduct. Most lignin-lignin condensation reactions involve the fifth carbon of the lignin aromatic ring, since it is the most reactive position, while nucleophilic reactions usually involve the alpha and beta carbons of the propyl sidechain.

Moisture, Ash, Elemental Analysis, and Klason Lignin

Moisture and ash determinations were routinely conducted on all steam-exploded wood samples, lignin isolates, and post-extracted residues (also called "pulps") - the latter results were obtained as part of Klason lignin determinations.

Typical, or average results for moisture and ash are presented in Table 32. The high moisture content of alkaline lignin isolates from steam-exploded aspen suggest greater hygroscopicity might arise from higher concentration of functional groups or higher surface area although the interpretation is complex because of a high ash content which could also explain increased hygroscopicity.

Elemental analyses were conducted on the steam-exploded Tulip poplar before and after extraction and on its ethanolic and lignin isolates. These values are summarized in Table 33. Corresponding information for the steam-exploded aspen (PSL), but for alkaline extraction only, are given in Table 34. Chua and Wayman (10) report the following elemental compositions for lignin which were extracted with 90% dioxane from which was autohydrolyzed in the range of 165-215°C for 0-120 minutes (cooking time):

Table 32
Moisture and Ash Analysis

Sample	% H_2O	% Ash
Steam-exploded Tulip Poplar	1.58	0.49
S.E.T.P. Pulp (after EtOH ext'n)	1.56	0.62
Ethanolic-Lignin Isolate (96 hrs.)	1.33	0.05
Alkaline-Lignin Isolate (S.E.T.P.) (NaOH 1- NaOH9)	2.82	1.39
Alkaline-Lignin Isolate (S.E.A.) (PSL 1 - PSL 10)	5.83	6.00

Notes:
S.E.T.P. = steam-exploded Tulip poplar
S.E.A. = steam-exploded Aspen

ASPEN AUTOHYDROLYSIS LIGNIN (10)

"Cooking Time"	% C	% H	% O
5 mins.	60.41	5.69	33.92
10	60.75	5.90	33.35
20	61.55	5.70	32.75
30	62.78	5.52	31.61
40	62.62	5.66	31.72
60	62.79	5.52	31.69
90	62.70	5.50	31.80
120	63.45	5.69	30.86

They also reported elemental analysis for a milled wood lignin (MWL): 59.5%C, 6.25%H, 34.25%O. The results are much closer to those observed with the aspen lignin isolates of this study. The investigators interpret the higher C-content results

Table 33

Elemental Analysis: Steam-Exploded Tulip Poplar and Lignin Isolates

Sample	% C	%H	%N	%O (by diff.)
Steam-exploded Tulip Poplar (Before extraction)	50.55	5.89	0.96	42.60
Steam-exploded Tulip Poplar (After ethanol extraction)	48.32	5.94	0.60	45.14
Ethanolic-Lignin Isolates (n = 9)	62.69	5.89	0.40	31.02
Alkaline-Lignin Isolates (n = 19)	59.17	5.51	0.64	34.68

Table 34

Elemental Analysis: Steam-Exploded Aspen and Lignin Isolates

Sample	%C	%H	%N	%O (By diff.)
Steam-exploded Aspen (PSL) (Before extraction)	46.4	5.7	<0.1	47.8
Steam-Exploded Aspen (PSL) (After Alkali extraction)	43.1	5.9	<0.1	50.9
Alkaline-Lignin Isolates (n = 11)	57.6	5.8	0.1	36.5

for their extracted lignins (and lower H- and O-contents) to (a) condensation reactions wich involve the elimination of water; and/or (b) the incorporation into the lignin of chemical entities having higher C to H/O ratios during autohydrolysis; and/or (c) the initial preferential removal of syringyl to guiacyl units at the shorter autohydrolysis times. The results obtained on both the aspen and Tulip poplar lignin isolates in this study suggest that the less extreme process conditions, during preparation by steam explosion by GIT and Stake leads to less significant deterioration in the quality of the post-processed lignin - although, as gel permeation chromatographic analysis suggests, the lignin obtained from the Stake-processed aspen indicates that substantial self-condensation exists for that treatment.

The results of Klason lignin content determinations are provided in Table 35 for both steam-exploded woods, aspen and Tulip poplar. The correlation between the yields obtained for ethanolic isolates (Table 25), 7.5% and for Klason lignin, 8.2%,

Table 35 Klason Lignin Content

	% Klason Lignin
Steam exploded Tulip Poplar (Untreated), (n = 5)	60.4
S.E.T.P. - After Ethanol Extraction, (n = 4)	52.2
"% Klason Lignin Extracted by Ethanol"	8.2
Steam-exploded Tulip Poplar (Untreated), (n = 5)	60.4
S.E.T.P. - After Alkali Extraction, (n = 6)	47.3
"% Klason Lignin Extracted by NaOH"	13.1
Steam-exploded Aspen (Untreated), (n = 8)	27.5
S.E.A. - After Alkali Extraction, (n = 8)	12.1
"% Klason Lignin Extracted by NaOH"	15.4

is good. However, the yields of alkaline lignin isolates (Table 26) with average recovery of 31.9%, contradict the Klason lignin extractables (13.1%) results which can only be attributed to incomplete digestion of the samples during the Klason lignin experiments, or that some type of acid-induced condensation/crosslinking reaction yielding insoluble products was initiated during laboratory processing. The Klason lignin contents for Tulip poplar are excessively high to begin with. The same materials, as analyzed earlier (8), were reported to have Klason lignin contents of 29.61 - 38.22% KL, for Tulip poplar processed @ 350 psig over periods of three (3) to seven (7) minutes.

GPC Determinations of Molecular Weight Properties

Gel permeation chromatograms were routinely run on the ethanolic and alkaline isolates obtained from the steam-exploded Tulip poplar. A single determination was made on the alkaline lignin isolate obtained from the steam-exploded aspen hardwood. The results of molecular weight determinations, number-average (Mn) and weight-average (Mw), as well as polydispersity (Mw/Mn) or molecular weight distribution, is given in Table 36. Typical chromatograms for the ethanolic and alkaline lignin isolates from Tulip poplar are superimposed in Figure 31. The GPC curve for the alkaline lignin isolate of the steam-exploded aspen was dramatically different in its elution times volume as shown in Figure 32. Indeed, it is unlikely that the Mw or polydispersity values have much validity because the pore sizes of the column were undoubtedly exceeded in the latter case.

It is apparent that the ethanolic lignin provides an exceptionally narrow, relatively low molecular weight polymer which, but for its low yield, would probably provide an ideal precursor for production of higher-value-added polymeric

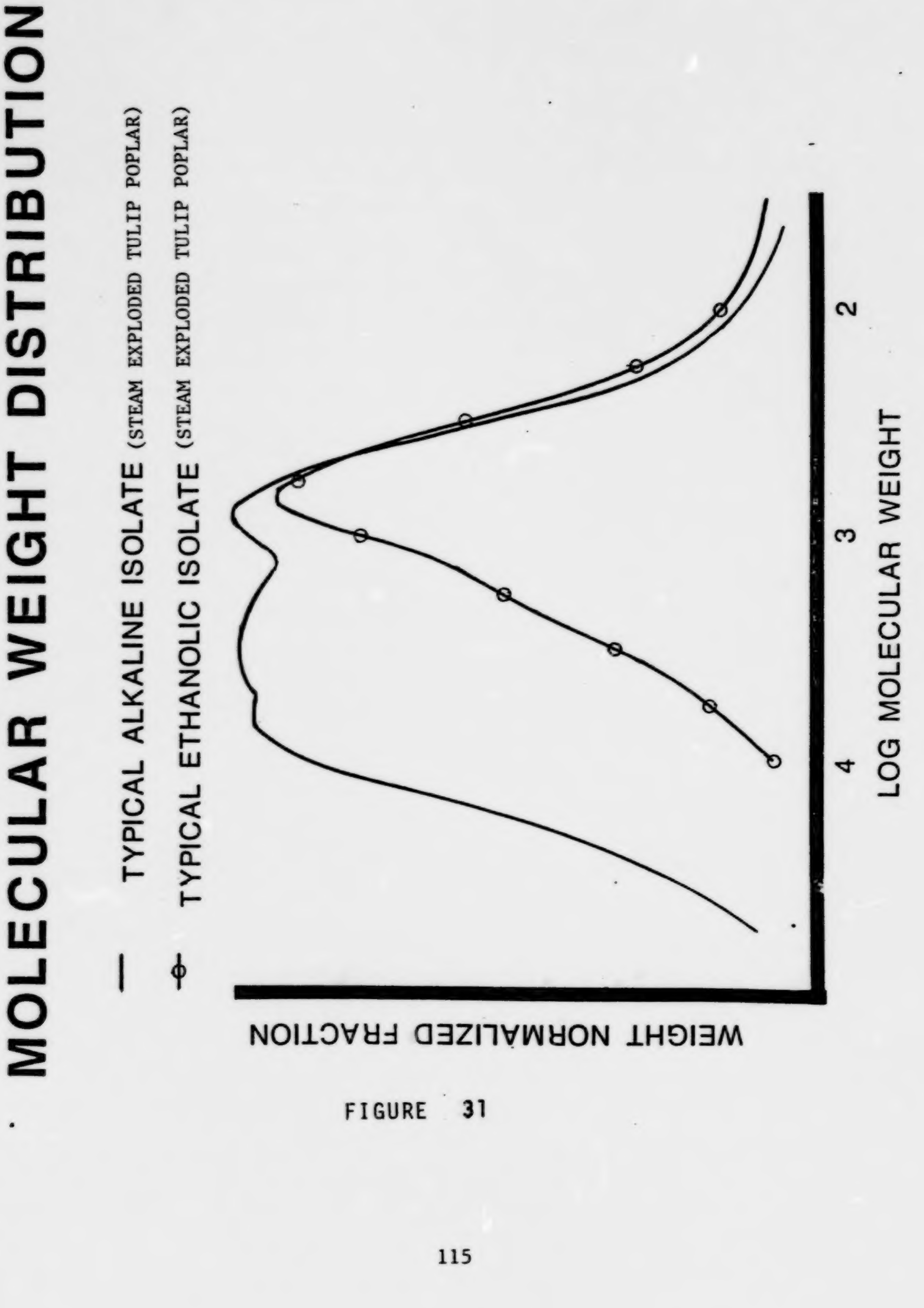

MOLECULAR WEIGHT DISTRIBUTION
TYPICAL ALKALINE ISOLATE (STEAM EXPLODED TULIP POPLAR)
TYPICAL ETHANOLIC ISOLATE (STEAM EXPLODED TULIP POPLAR)
WEIGHT NORMALIZED FRACTION
LOG MOLECULAR WEIGHT
4
3
2

FIGURE 31

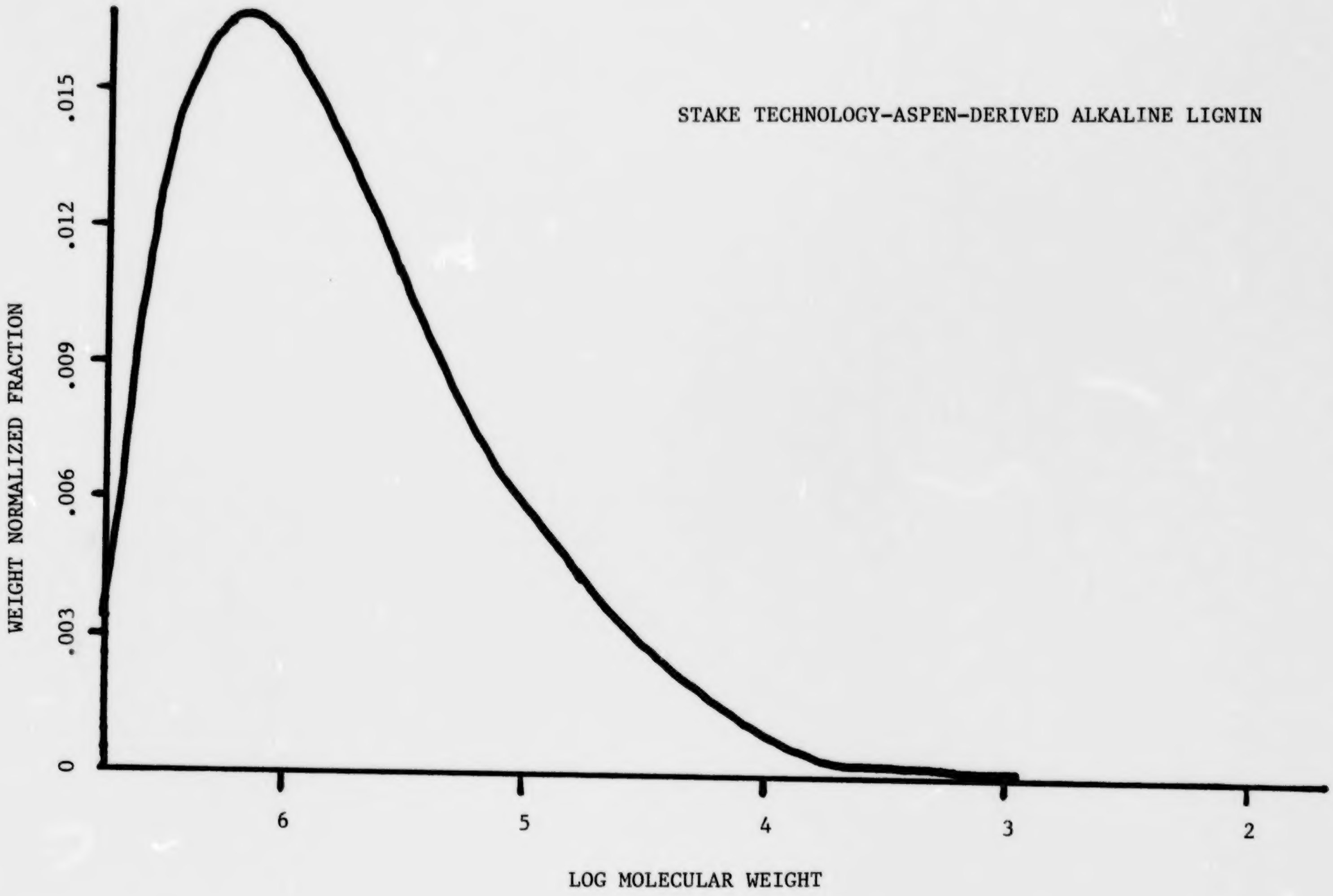


FIG. 32 MOLECULAR WEIGHT DISTRIBUTION: LIGNIN (ASPEN)

derivatives. The higher polydispersity of the alkaline isolate is indicative of the solubilization of branched components of the total lignin network in the steam-exploded Tulip poplar. The exceptionally high polydispersity of the alkaline isolate of aspen suggests very extensive condensation within the lignin network. In fact, the branching is so extensive as to suggest that one has produced a pseudo-solution, perhaps a micro-gel, although no clogging of the GPC column was evident.

Table 36

Molecular Weight and Polydispersity of Lignin Isolates

	Mw	Mn	Mw/Mn
Ethanolic lignin (Tulip poplar) (n = 5)	1,379	939	1.47
Alkaline lignin (Tulip poplar) (n = 6)	2,333	859	2.72
Alkaline lignin (Aspen)	88,311	2,081	42.4

Spectroscopic Analysis

Spectroscopic characterization of lignin was conducted with infrared spectroscopy, ultraviolet spectroscopy, C^{13} NMR spectroscopy, and proton magnetic resonance spectroscopy.

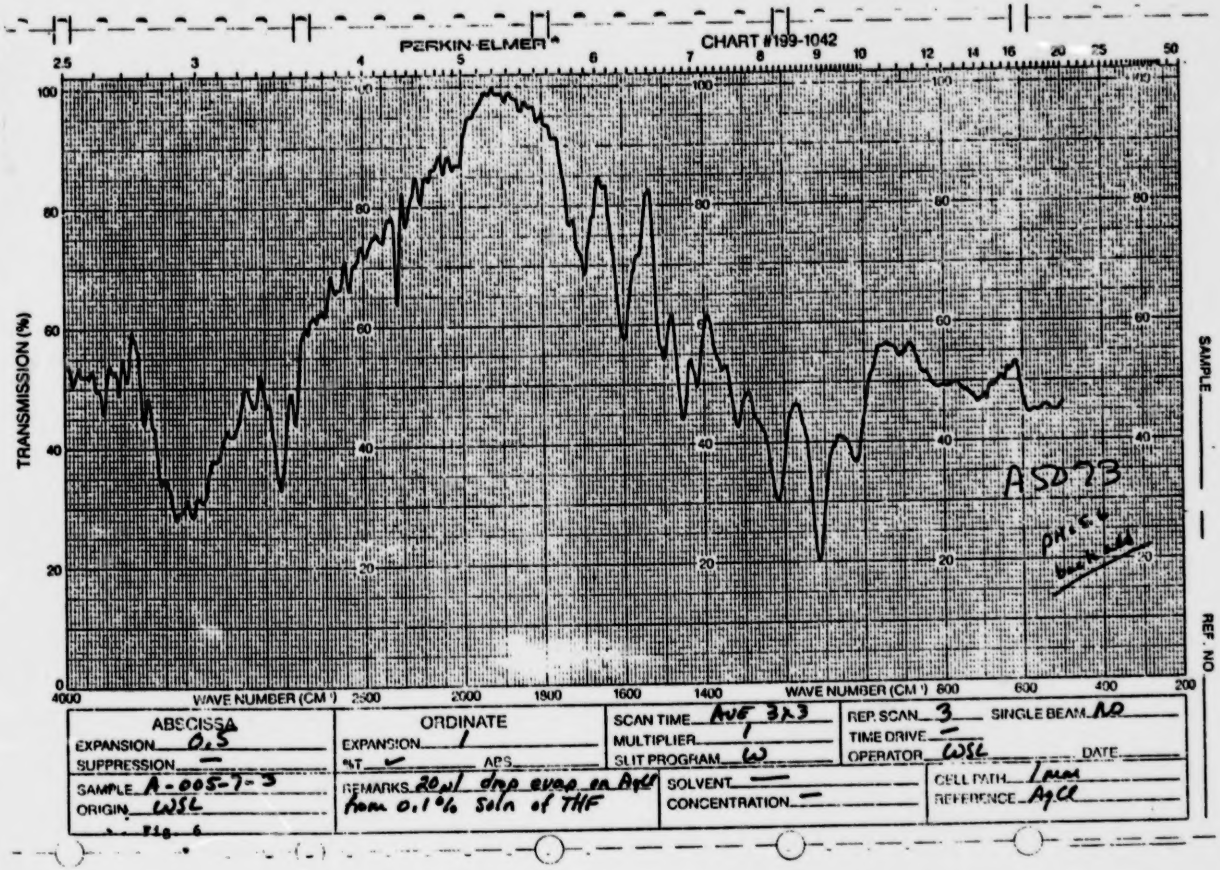
The major advantage of the IR spectra, besides correlation of isolates qualitatively with each other and "known" lignin spectra, was to monitor the stability (or changes in functionality) of the lignin isolates during work-up. Significant spectral differences were noted in the dark, friable isolates (e.g., SH-016) and light, powdery isolates (e.g., SH-015).

Gross functionality, indicative of lignin, is evident in the infrared region in apparent absorptions at the following wavelengths in Figure 33:

2.88	microns	Aromatic hydroxyl, -OH
3.29-3.43		Methyl group, Aromatic C-H
5.65-5.81		Non-quinonoid carbonyls
5.96/6.04		Unsymmetrical quinonoid carbonyl
6.31		Aromatic C=C band stretching
6.73		Tri- and tetra-substituted Ar nuclei
7.02-7.90		C-H and O-H bending
8.17		C-O-C bending
8.48		Symmetrical C-O-C bending
9.0		Aromatic hydroxyl and ether
9.62		Aromatic ether
10.1		Double bond, C=C
10-14		Aromatic ring substitution

Ultraviolet spectra (e.g., Figure 34) corresponded to reported values of adsorption maxima in other lignin studies and of related (model) corresponds e.g. a maximum in the region of 273 nm (in tetrahydrofuran) corresponds well to a value of 277nm in ethanol for spruce-derived lignin (11).

The only study, other than that of this investigation, on the structure of lignin as evident in ^{13}C NMR spectroscopy and proton magnetic resonance (PMR) spectroscopy was conducted on lignin extracted from milled wood and steam-exploded *Pinus radiata*, a softwood (11). An exhaustive interpretation of the results of our data was not possibe. The most significant difference between our results and those on the softwood lignin is the presence of extensive adsorption peaks from 103-107 and @



ABSCISSA
EXPANSION 0.5
SUPPRESSION —

ORDINATE
EXPANSION 1
%T ✓ ABS

SCAN TIME AVE 3x3
MULTIPLIER 1
SLIT PROGRAM W

REP. SCAN 3 SINGLE BEAM NO
TIME DRIVE —
OPERATOR WSL DATE

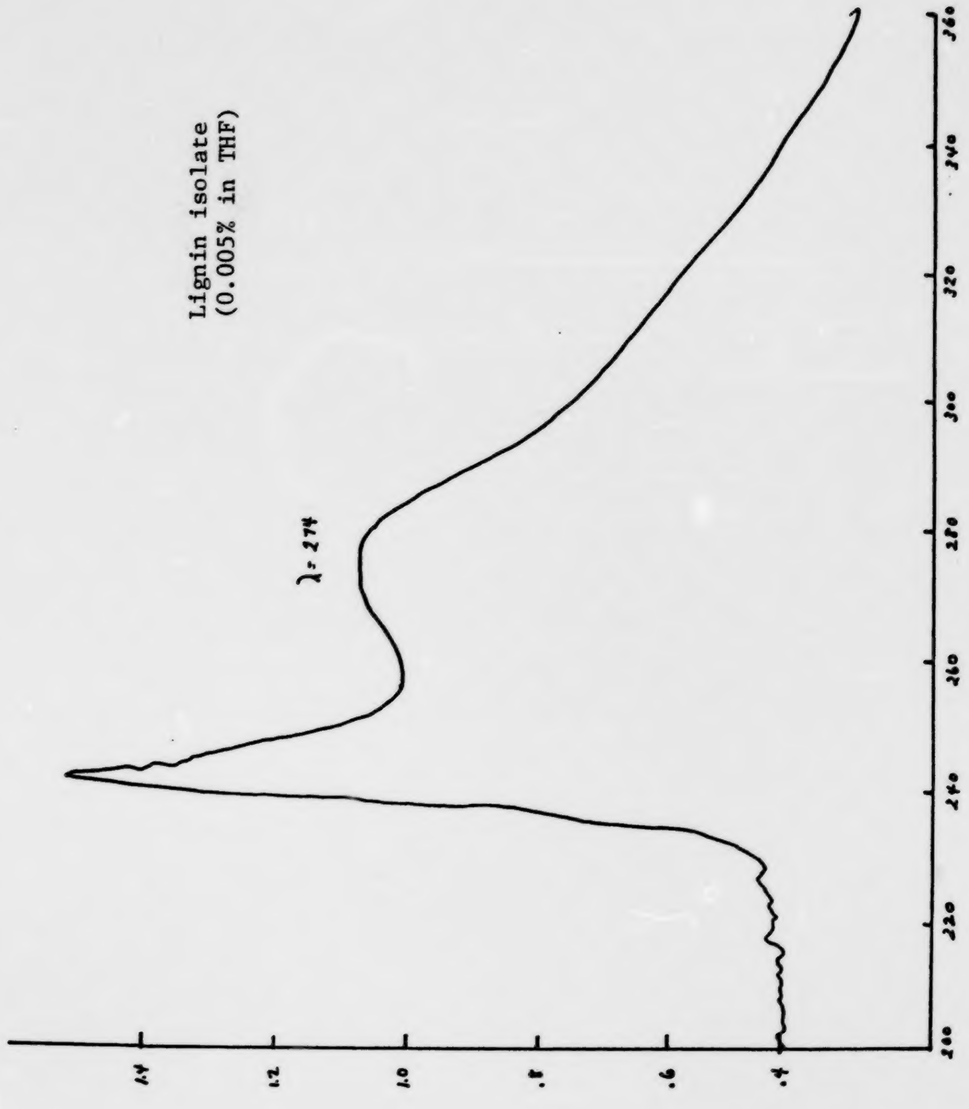
SAMPLE A-005-7-3
ORIGIN WSL
Fig. 6

REMARKS 20 μl drop evap on AgCl from 0.1% soln of THF

SOLVENT —
CONCENTRATION —

CELL PATH 1 mm
REFERENCE AgCl

FIG. 33 TYPICAL INFRARED SPECTRUM: ETHANOLIC LIGNIN (FROM STEAM EXPLODED TULIP POPLAR)



UV SPECTRUM OF LIGNIN

FIG. 34 TYPICAL UV SPECTRUM: ETHANOLIC LIGNIN (TULIP POPLAR) (in tetrahydrofuran)

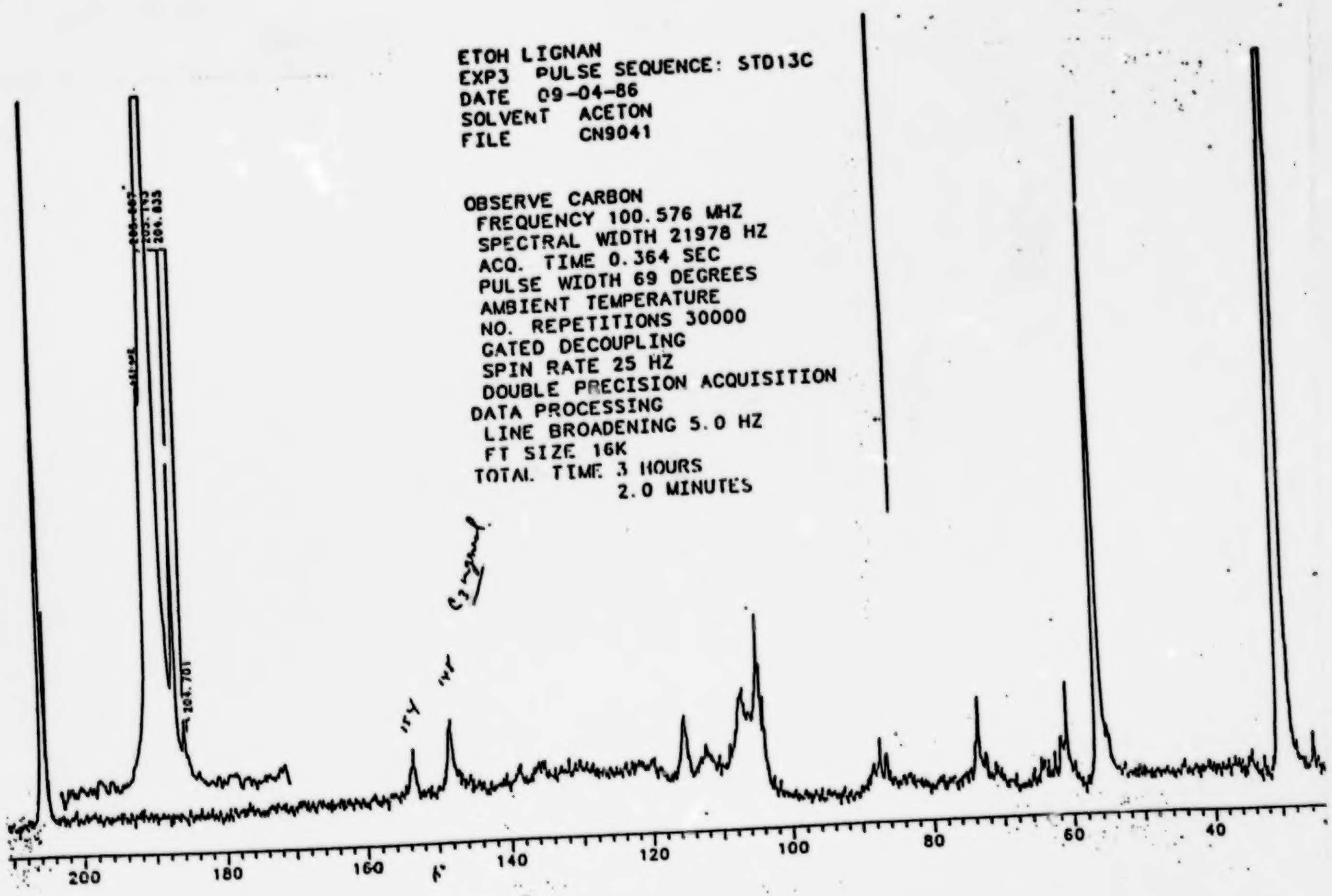
107-109 which are absent in the softwood lignin. These may be attributable to different aromatic carbon adsorptions, specifically to the sinapyl alcohol-type (or syringaldehyde-precursor) of structure in hardwood lignin where the aromatic nucleus is completely tetrasubstituted. A representative C^{13} NMR spectrum for ethanolic lignin isolate is presented in Fig. 35.

The proton magnetic resonance spectra (Figure 36) is characterized by hydroxyl group and methoxyl group absorptions from 3-4 ppm and a weaker methylene/methyl peaks @ 0.95 and 1.28 ppm.

Electrochemical Analysis

The procedure described in the experimental sections has been used to determine functionality of humic acids and humic-like substances. In the early stages of this experiment it became evident that the pristine lignin has a functional group distribution unlike that of humic substances. The problem of putting the pristine lignin into solution has been mentioned. Humic substances are readily dissolved. The pristine lignin was dissolved in alkali and then the alkali was neutralized by adding an equivalent amount of acid, in effect creating a neutral salt solution. Once the titration was initiated it was observed that the lignin precipitated from solution. The results, therefore, may be used only as an approximation of functionality.

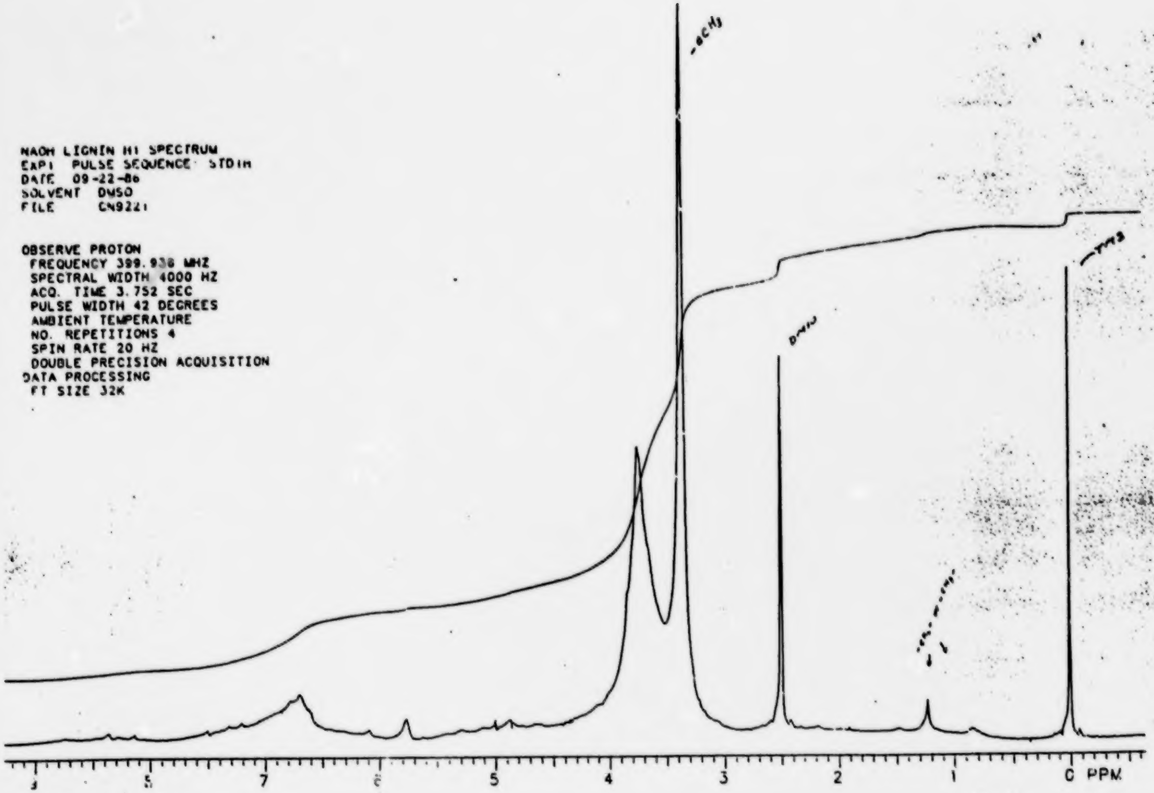
Assuming that the results of these experiments are correct a computer program developed by Perdue is capable of estimating the aromatic and aliphatic carbon content of a humic sample (or lignin, being humic-like) using the following data: elemental composition, concentration of carboxyl and carbonyl groups and



```
ETOH LIGNAN
EXP3  PULSE SEQUENCE: STD13C
DATE  09-04-86
SOLVENT  ACETON
FILE     CN9041

OBSERVE CARBON
 FREQUENCY 100.576 MHZ
 SPECTRAL WIDTH 21978 HZ
 ACQ. TIME 0.364 SEC
 PULSE WIDTH 69 DEGREES
 AMBIENT TEMPERATURE
 NO. REPETITIONS 30000
 GATED DECOUPLING
 SPIN RATE 25 HZ
 DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 5.0 HZ
 FT SIZE 16K
TOTAL TIME 3 HOURS
           2.0 MINUTES
```

FIG. 35 REPRESENTATIVE C^{13} NMR SPECTRUM: LIGNIN (ETHANOLIC ISOLATE)



```
NAOH LIGNIN H1 SPECTRUM
EXP1  PULSE SEQUENCE  STD1H
DATE  09-22-86
SOLVENT  DMSO
FILE     CN9221

OBSERVE PROTON
 FREQUENCY 399.938 MHZ
 SPECTRAL WIDTH 4000 HZ
 ACQ. TIME 3.752 SEC
 PULSE WIDTH 42 DEGREES
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4
 SPIN RATE 20 HZ
 DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 FT SIZE 32K
```

FIG. 36 REPRESENTATIVE PMR SPECTRUM: LIGNIN (ALKALINE ISOLATE)

molecular weight (12). This model allows us to compare the various pristine lignin isolates. Van Krevelen-like diagrams provide a visual means for this comparison. The results of electrochemical analysis are given in Tables 37 and 38 for ethanolic lignin and alkaline lignin, respectively. Based on the structural model employed, it can be seen from the Van Krevelen diagrams (Figure 37 and 39) that the carbon-types in both forms of lignin are relatively equally distributed among aromatic carbon, aliphatic carbon, and "excess" carbon (the latter category is used to assure mass balance in the model and specifically includes other unspecified types of carbon - or hydrogen and unsaturation, e.g., as found in esters, amides, alkenes, quinones, etc.). In the case of hydrogen, (Fig. 38) functional group analysis showed phenolic hydroxyl group concentration to be relatively significant although carboxylic acid concentration was quite low in relation to humic acids (understandably), since the latter are products of natural oxidative degradation. However, the Van Krevelen diagrams and analysis demonstrate that most of the hydrogen is associated with alkyl carbon groups, indicating extensive aromatic ring condensation and little hydroxyl functionality. These results provide some support for the limitation on adsorption capacity observed with the lignin isolates.

Surface area and Density Analysis

The bulk or **apparent** bulk densities of steam-exploded wood are presented in Table 39.

```
                      Structural Features of EtOH Composite

**** Composition Data ****                 ** Parameter Estimation Data **
         %(w/w)      mmol/g                   Ratio      Lower      Upper
 C        62.50       52.08                   H/C-AL     1.000      3.000
 H         5.60       56.00                   H/C-AR     0.000      0.833
 N         0.50        0.36                   H/C-XS     0.000      1.500
 O        31.40       19.62                   U/C-AL     0.000      0.250
 S         0.00        0.00                   U/C-AR     0.667      0.667
 COOH      n.a         2.11                   U/C-XS     0.500      1.000
 C=O       n.a         0.00
 Molecular Wt :         800
 Maximum F-ar :       0.674

        Statistical Summary after 1000 Viable Solutions in  3550 Attempts

INCR  H/C-AL  H/C-AR  H/C-XS  U/C-AL  U/C-AR  U/C-XS   C-AL    C-AR    C-XS
 0       20     158     270      88    1000     157      0     130     179
 1       23     135     193     112       0     133     35     151     197
 2       55     128     126     134       0     115    143     156     171
 3      120     120     101     116       0      96    443     177     170
 4      175     101      70      94       0      86    287     161     133
 5      170      68      61      89       0      89     83     159      76
 6      151      69      75     100       0      94      9      66      47
 7      112      67      52      95       0      82      0       0      20
 8      103      60      39      84       0      82      0       0       7
 9       71      94      13      88       0      66      0       0       0

                     Most Probable Distribution of Carbon

Carbon Type     Med(mmol/g)     Mean(mmol/g)      Std Dev       Mole Fract.

COOH+C=O           2.11            2.11            n.a.           0.041
C-AL              18.61           18.80            4.59           0.361
C-AR              16.79           16.59            9.02           0.319
C-XS              13.22           14.58            9.50           0.280

                             Correlation Matrix

        H/C-AR  H/C-XS  U/C-AL  U/C-AR  U/C-XS   C-AL    C-AR    C-XS
H/C-AL  -0.198  -0.381  -0.334   0.000   0.035  -0.235   0.365  -0.233
H/C-AR    ..    -0.059  -0.036   0.000  -0.293  -0.197   0.031   0.066
H/C-XS    ..      ..    -0.035   0.000  -0.611  -0.516  -0.095   0.339
U/C-AL    ..      ..      ..     0.000  -0.088   0.460  -0.175  -0.056
U/C-AR    ..      ..      ..      ..     0.000   0.000   0.000   0.000
U/C-XS    ..      ..      ..      ..      ..     0.691   0.027  -0.359
 C-AL     ..      ..      ..      ..      ..      ..    -0.147  -0.343
 C-AR     ..      ..      ..      ..      ..      ..      ..    -0.879
```

TABLE 37 STRUCTURAL FEATURES OF ETHANOLIC COMPOSITE LIGNIN ISOLATE (ELECTROCHEMICAL FUNCTIONAL GROUP ANALYSIS)

```
                         Structural Features of NaOHI

  **** Composition Data ****              ** Parameter Estimation Data **
        %(w/w)     mmol/g                    Ratio      Lower      Upper
   C     61.40     51.17                     H/C-AL     1.000      3.000
   H      5.50     55.00                     H/C-AR     0.000      0.833
   N      0.50      0.36                     H/C-XS     0.000      1.500
   O     32.60     20.37                     U/C-AL     0.000      0.250
   S      0.00      0.00                     U/C-AR     0.667      0.667
   COOH    n.a      0.93                     U/C-XS     0.500      1.000
   C=O     n.a      0.00
   Molecular Wt :   1000
   Maximum F-ar :  0.701

      Statistical Summary after  200 Viable Solutions in   660 Attempts

INCR  H/C-AL  H/C-AR  H/C-XS  U/C-AL  U/C-AR  U/C-XS    C-AL    C-AR    C-XS
 0       6      38      69      23     200      23       0      20      30
 1       1      20      41      22       0      23       6      28      50
 2       7      21      28      22       0      20      31      30      38
 3      26      27      17      23       0      23      97      40      29
 4      24      18      10      18       0      17      51      34      29
 5      36      16      11      24       0      15      14      36      12
 6      35      13       9      20       0      11       1      12      10
 7      31      16       8      16       0      23       0       0       2
 8      20       9       6      13       0      19       0       0       0
 9      14      22       1      19       0      26       0       0       0

                   Most Probable Distribution of Carbon

  Carbon Type     Med(mmol/g)    Mean(mmol/g)      Std Dev       Mole Fract.

  COOH+C=O           0.93           0.93            n.a.           0.018
  C-AL              18.58          18.72            4.26           0.366
  C-AR              17.85          17.53            8.68           0.343
  C-XS              12.69          13.99            9.04           0.273

                           Correlation Matrix

         H/C-AR   H/C-XS   U/C-AL   U/C-AR   U/C-XS    C-AL     C-AR     C-XS
 H/C-AL  -0.188   -0.504   -0.203    0.000    0.096   -0.142    0.411   -0.328
 H/C-AR    ..      0.038   -0.041    0.000   -0.380   -0.294    0.067    0.074
 H/C-XS    ..       ..     -0.021    0.000   -0.592   -0.539   -0.214    0.459
 U/C-AL    ..       ..       ..      0.000   -0.201    0.360   -0.054   -0.118
 U/C-AR    ..       ..       ..       ..      0.000    0.000    0.000    0.000
 U/C-XS    ..       ..       ..       ..       ..      0.696    0.044   -0.371
  C-AL     ..       ..       ..       ..       ..       ..     -0.159   -0.319
  C-AR     ..       ..       ..       ..       ..       ..       ..     -0.885
```

TABLE 3B STRUCTURAL FEATURES OF ALKALINE LIGNIN ISOLATE (ELECTROCHEMCIAL FUNCTIONAL GROUP ANALYSIS)

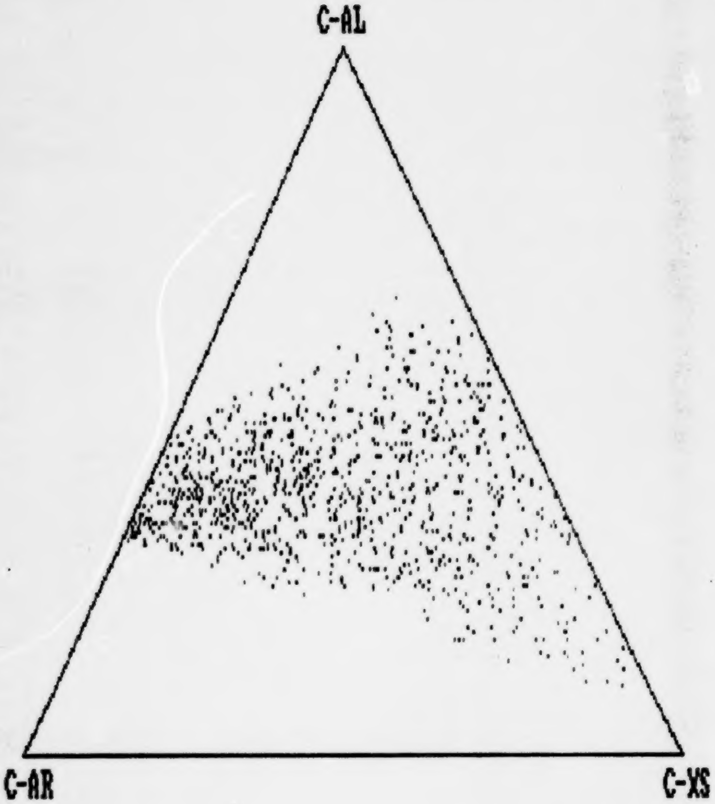


FIG. 37 VAN KREVELEN DIAGRAM (CARBON): ETHANOLIC LIGNIN

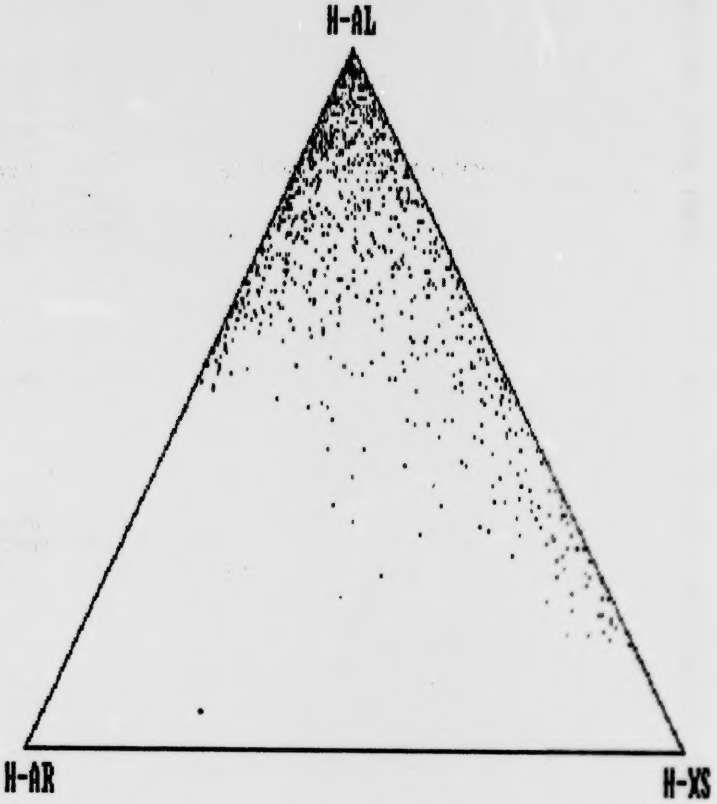


FIG.38 VAN KREVELEN DIAGRAM (HYDROGEN): ETHANOLIC LIGNIN

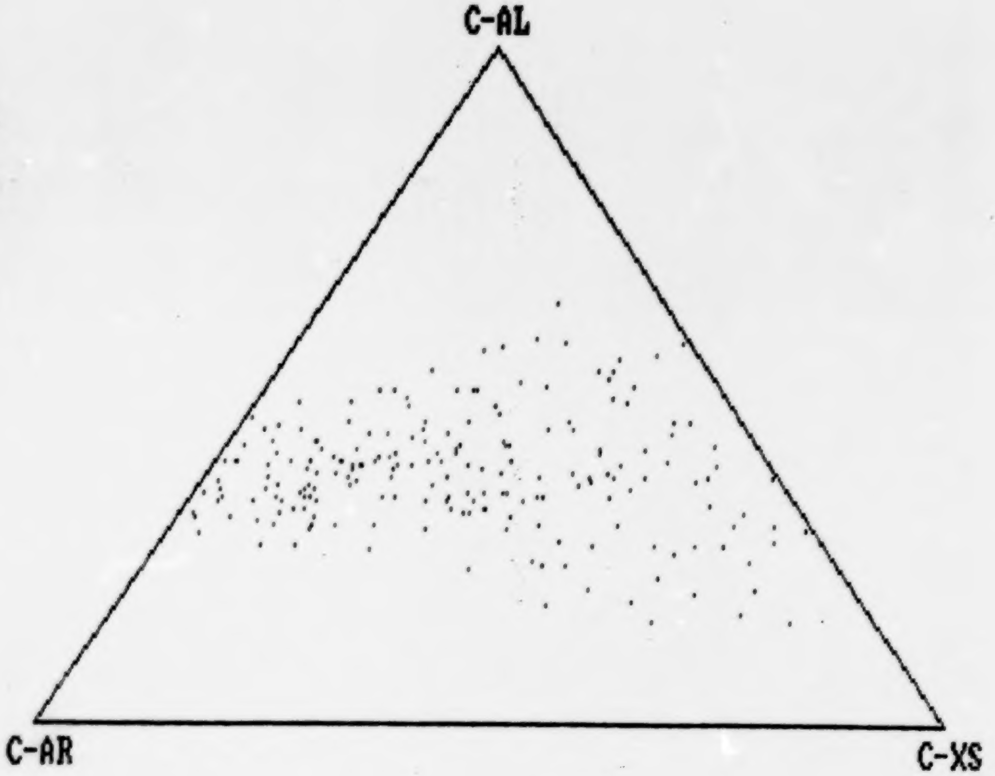


FIG. 39 VAN KREVELEN DIAGRAM (CARBON): ALKALINE LIGNIN ISOLATE

Table 39

Apparent Bulk Densities

Sample	Bulk Density	Notes
Steam-exploded Tulip Poplar	1.85 kg/l	3% H_2O
Steam-exploded Aspen	2.33 kg/l	1% H_2O
Ethanolic-Lignin (Tulip poplar) (n = 4)	0.336 kg/l	PH-046
Alkaline-Lignin (Tulip poplar) (n= 4)	0.606 kg/l	NaOH 1

BET Surface Area Analyses were conducted on various samples (using krypton and nitrogen). Results are recorded in Table 40.

Table 40

BET Suface Area Analyses

Sample	Gas	SA(m2/g)	Notes
Ethanolic-lignin (Tulip poplar)	N_2	30.19	PH-046
Alkaline-lignin (Tulip poplar)	N_2	0.91	NaOH-1
Alkaline-lignin (Tulip poplar)	Kr	0.14	NaOH-1
Steam-exploded (Tulip poplar)	N_2	1.46	$^-$10 mesh

Thermal Analysis

Samples of A-005-7-2 and A-005-7-4 were analyzed by differential scanning calorimetery and thermogravimetric analysis through a maximum of 260°-280°C. Except for endothermic evaporation of water and incipient decomposition beginning near 180°C, there are no marked transitions and one may conclude that lignin is relatively thermostable in terms of primary bond integrity. However, that conclusion is subject to the qualification that crosslinking (and loss of functionality, i.e., adsorptive capacity) may be masked. See Figures 40 and 41 for representative thermograms.

The results of calorimetric determination on the steam-exploded tulip poplar, ethanolic lignin (PH-046) and alkaline lignin (NaOH) are presented in Table 41. It is clear that lignin is the major energetic component in steam-exploded wood and provides a useful combustible matrix for hazardous waste isolation and disposal, subject to dewatering efficiency.

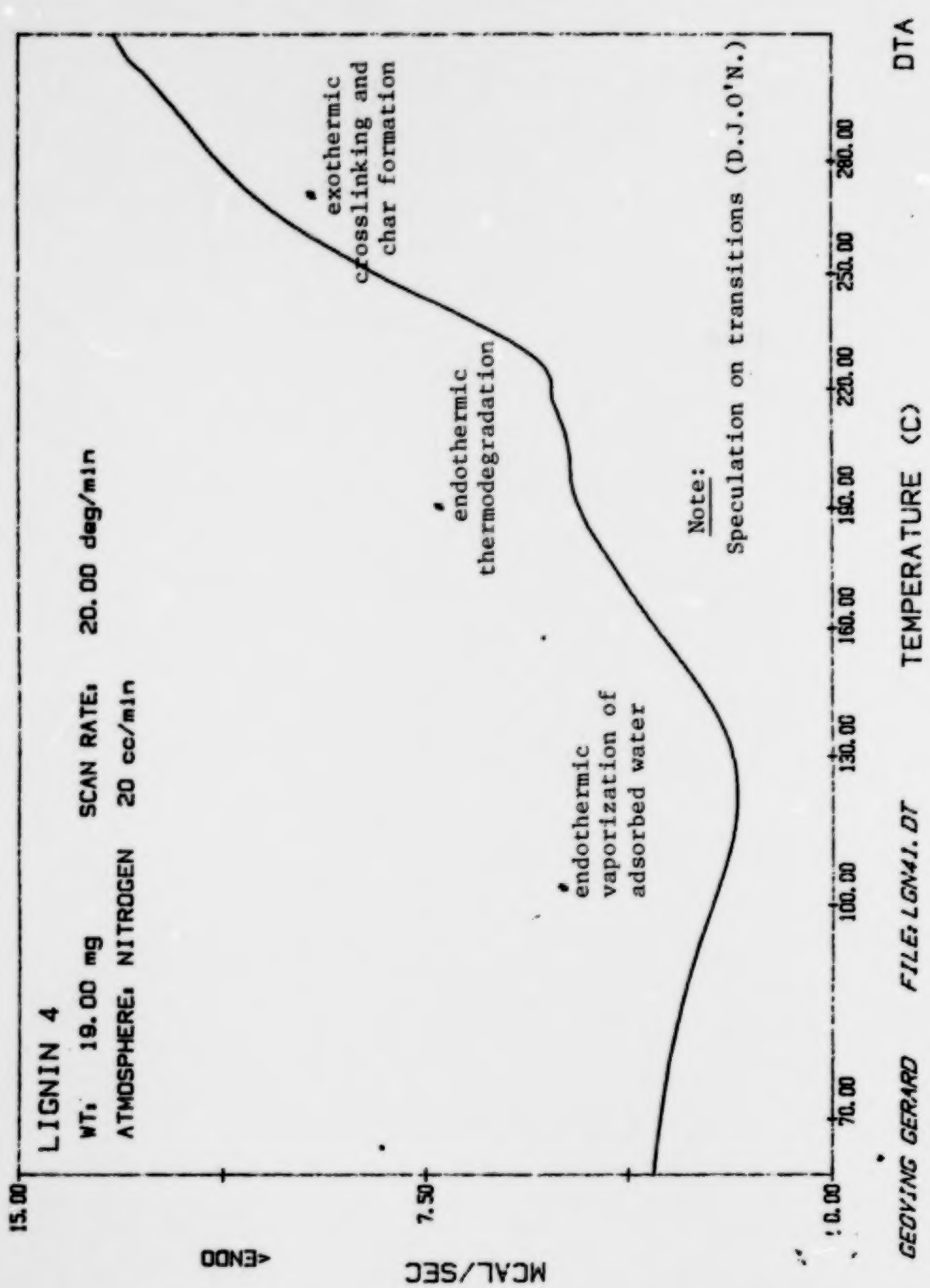


FIGURE 40 TYPICAL DSC THERMOGRAM: LIGNIN

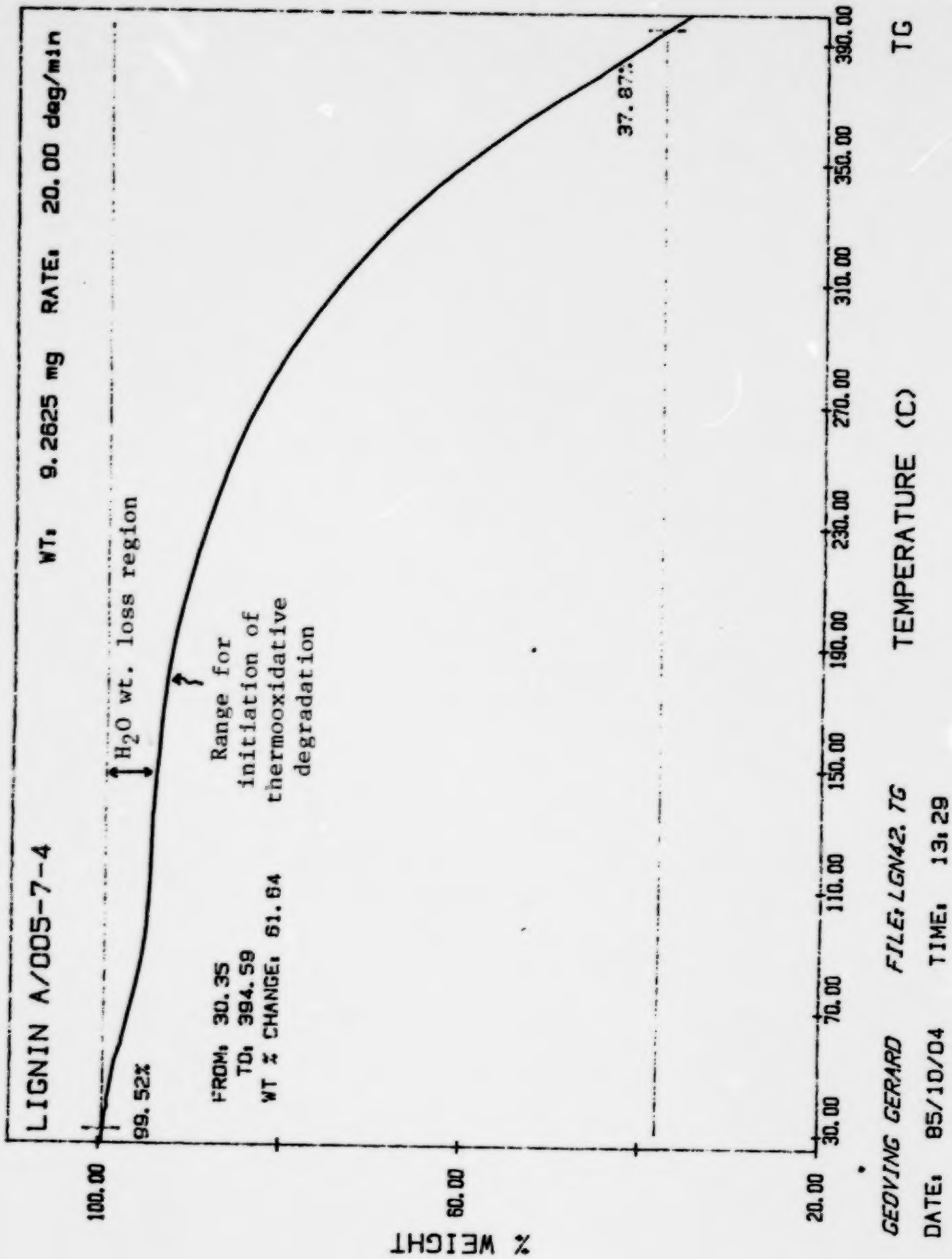


FIGURE 41 TYPICAL TGA THERMOGRAM: LIGNIN

Table 41

Heats of Combustion

(Higher Heating Value; Dry weight basis)

PH046: Ethanol-extracted Lignin

(1) 10830

(2) 10823

10827 Btu/lb average, as is

11410 Btu/lb dry basis

NaOH2: Alkali-extracted Lignin

(1) 10371

(2) 10328

10350 Btu/lb average, as is

10455 Btu/lb dry basis

Steam-exploded Wood

(1) 8133

(2) 8069

8100 Btu/lb average, as is

8230 Btu/lb dry basis

Adsorption Behavior of Pristine Lignin with Selected Model Hazardous Waste Compounds

Kinetic Studies

The kinetic studies were confined to one set of conditions, an ethanolic lignin isolate (PH047) of low yield and molecular weight and of narrow molecular weight distribution, and of relatively high particle size (30 X 40 mesh) equilibrated at pH of 4.0 and a temperature of 19°C for four days. The major advantage of this series of experiments was to establish the equilibrium time required for measurements of adsorptive capacity.

The results of the kinetic studies on the organic compounds is shown graphically in Figures 42 to 45, where results for aniline and phenol are displayed on one graph (Figure 42). isophorone and naphthalene are displayed on another (Figure 43), trichloroethylene and 2,4-D results appear in Figure 44 and the rate of adsorption is indicated for pentachlorophenol and bis(2-ethylhexyl)phthalate in Figure 45. The individual analytical results are tabulated in Table 42.

It is apparent from these data and figures that removal of the model organic compounds levels off within two days, undetectable limits being reached after only one day in the cases of bis(2-ethylhexyl)phthalate and pentachlorophenol (Figure 45).

It appeared reasonable that future adsorption studies be conducted with allowance for four days to achieve equilibrium. Since a large particle size (30/40 mesh) was used, it may be anticipated that the time required for achieving equilibrium with

Table 42 Concentrations of Model Compounds in the Supernatant After adsorption on the Pristine Lignin (ppm)

Time	Aniline	Phenol	Isophorone	Naphthalene	Pentachlorophenol	Bis-(EtHex) phthalate	2,4-D	Trichloro ethylene
0 hr.	5.000	5.000	1.560	1.300	1.540	1.560	1.250	2.500
1 hr.	4.09	2.62	1.66	0.97	0.70	0.33	1.08	1.97
	3.20	2.56	1.37	0.74	0.70	0.36	1.27	1.55
2 hr.	3.29	2.73	1.29	0.61	0.54	0.29	1.21	1.54
	3.34	2.50	1.41	0.65	0.52	0.23	1.28	1.52
4 hr.	3.75	2.56	1.39	0.63	0.49	0.22	1.05	1.93
	4.09	2.66	1.49	0.65	0.49	0.23	1.28	1.52
8 hr.	4.14	2.48	1.38	0.57	BDL*	0.14	0.74	0.36
	3.97	2.22	1.61	0.64	BDL	0.14	1.03	1.78
1 day	3.52	1.94	1.31	0.56	BDL	0.18	0.67	1.63
	3.25	2.38	1.23	0.51	BDL	BDL	--**	1.73
2 days	1.56	2.26	1.22	0.53	BDL	BDL	0.63	1.97
	2.62	2.16	1.06	0.41	BDL	--	--	1.94
4 days	2.88	1.77	1.16	0.48	BDL	BDL	0.57	1.45
	1.47	2.16	1.02	0.45	BDL	BDL	0.65	--
4 days**	0.71	2.05	0.68	0.21	BDL	BDL	0.60	0.54
	1.28	2.06	0.81	0.24	BDL	BDL	0.75	1.26

* BDL - Below detection limit

** Samples were lost

*** Lignin dose was 0.75g for organic mixture, 0.5g for 2,4-D, and metal kinetics study.

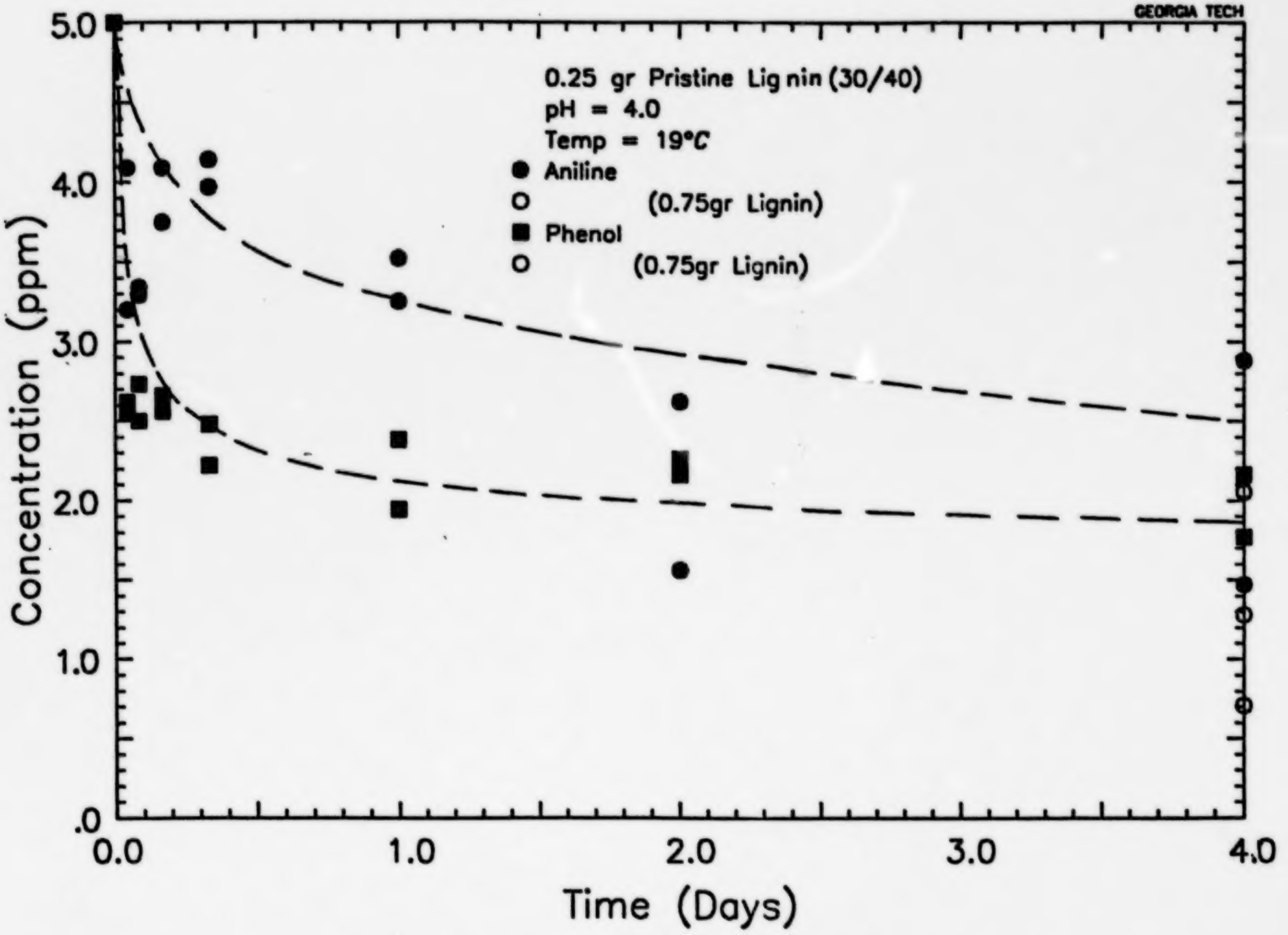


Figure 42 Kinetic Studies for the Adsorption of Organic Compounds on Pristine Lignin

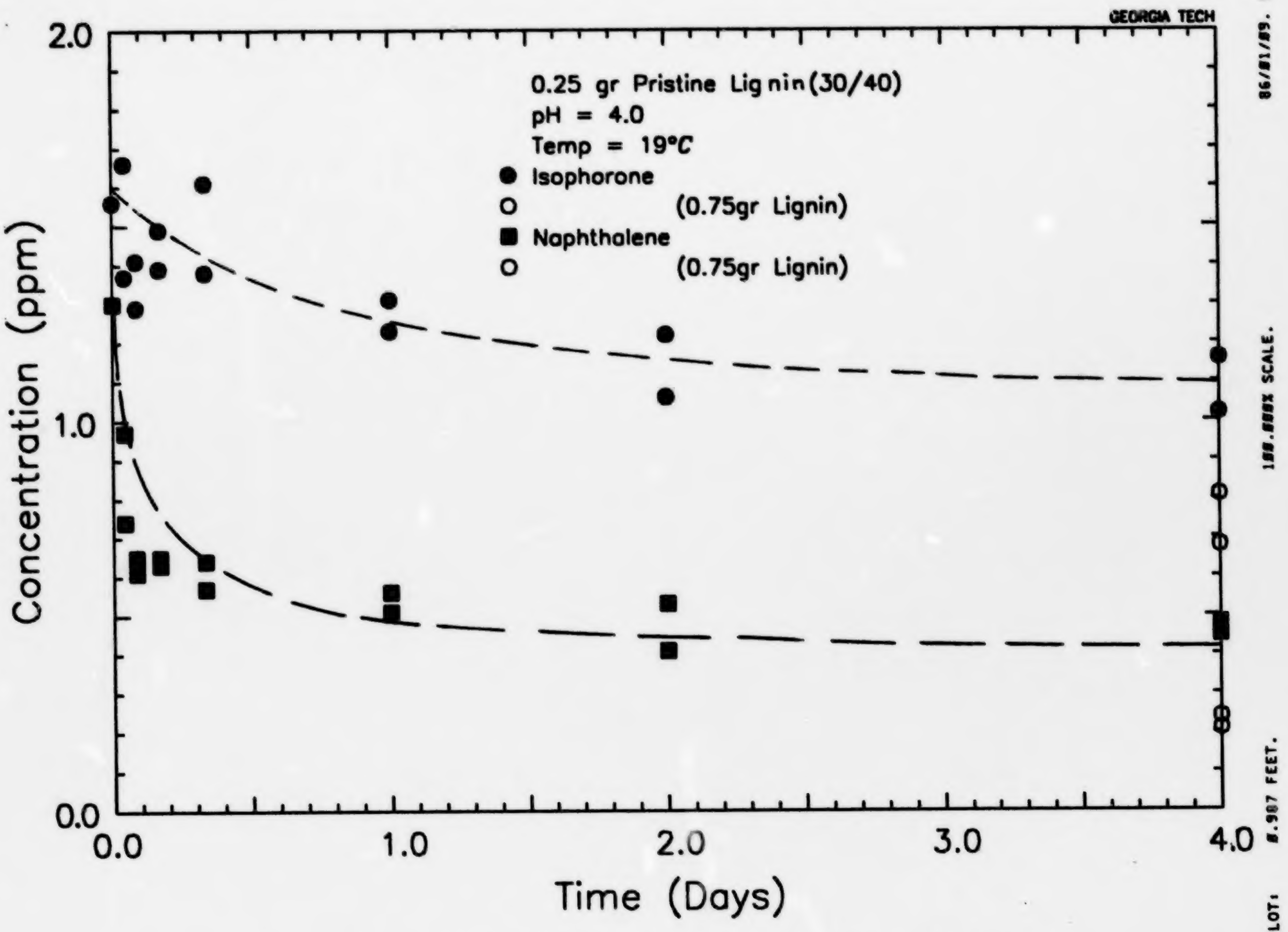


Figure 43 Kinetic Studies for the Adsorption of Organic Compounds on Pristine Lignin

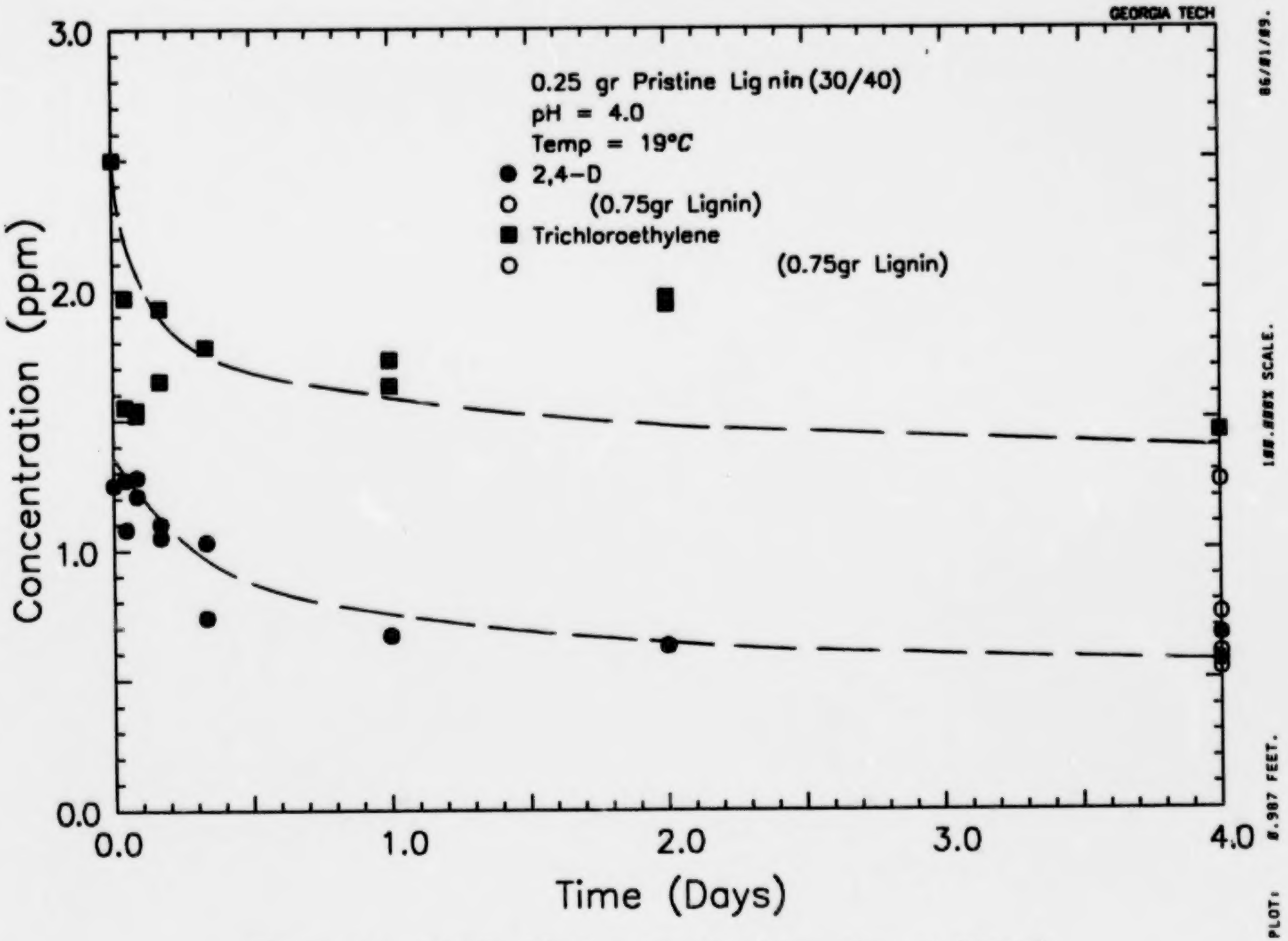


Figure 44 Kinetic Studies for the Adsorption of Organic Compounds on Pristine Lignin

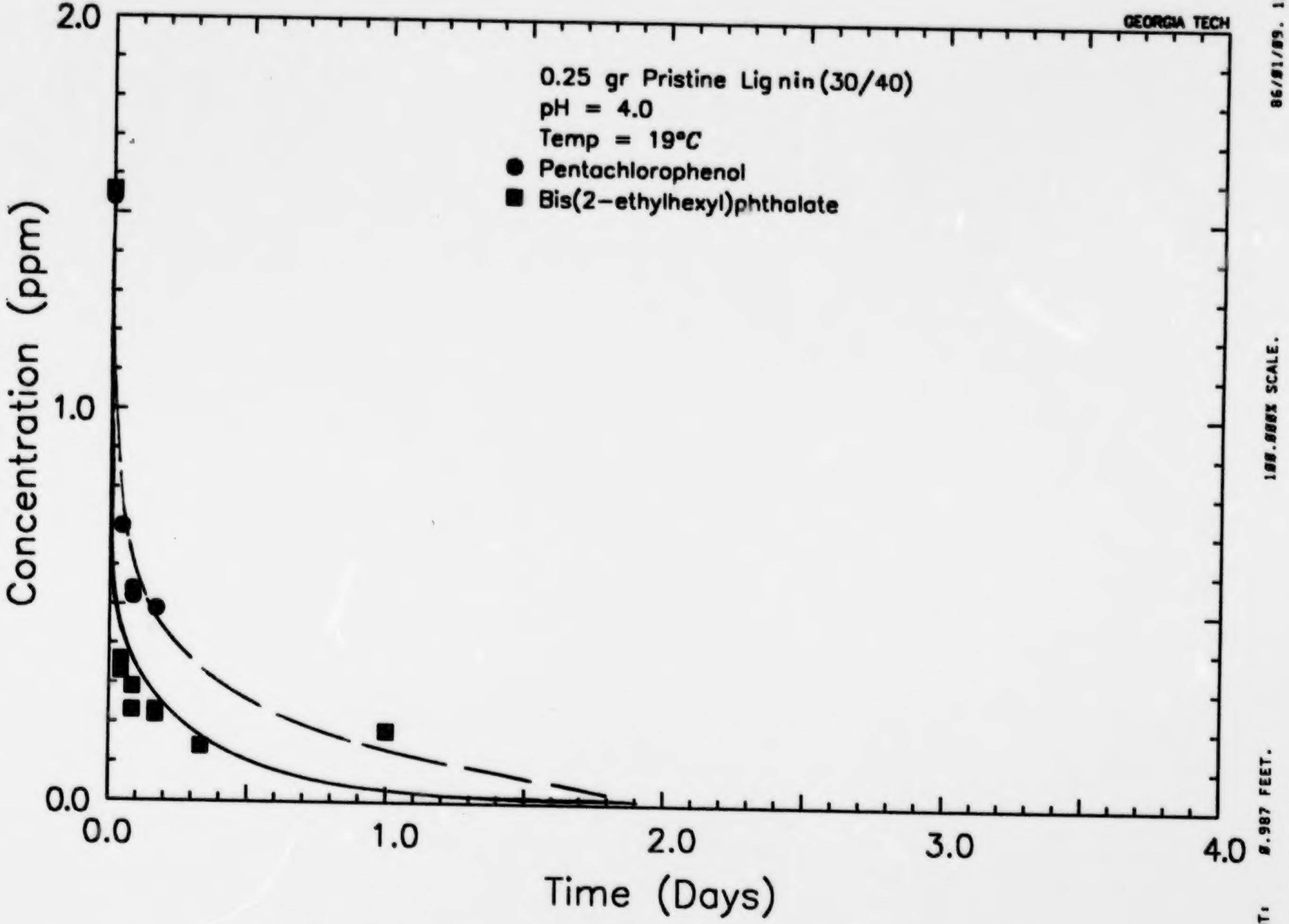


Figure 45 Kinetic Studies for the Adsorption of Organic Compounds on Pristine Lignin

smaller particle sizes (e.g., 40/60 and 80/100 mesh ranges) would be substantially less than four (4) days.

Based on this study, preliminary values of adsorptive capacities were estimated to be 5g/kg lignin (ethanolic PH047) for the seven-compound mixture and 0.3g/kg for 2,4-D. These initially low values were thought to be attributable to a low surface area availability with 30/40 mesh particle size and to the low equilibrium concentrations employed in this study.

The results of the kinetic studies of lead and chromium are presented in Figure 46 and are tabulated in Table 43. The time required for achieving equilibrium is less than twelve (12) hours for chromium, while lead requires less than forty-eight hours. One may conclude that an equilibrium time of four (4) days would also be sufficient for adsorption studies of heavy metals. An adsorption capacity of 1.3 g/kg was estimated for lead and chromium under these conditions.

As a final observation, it was noted that an increase in adsorption of model compounds, both organic and inorganic, was achieved with a higher charge of lignin (0.75g), suggesting the possibility of rapid saturation of adsorption sites on the surface of the adsorbent and little penetration (porosity) of the adsorbent.

Adsorption Size Studies

The results of an initial size study experiments for three different particle size fractions of ethanolic lignin isolates and one comparable fraction of alakaline isolate are presented in Table 44. As noted in this table, all runs on model compounds were questionable with the exception of the inorganic compounds

Table 43 **Kinetic Study: Concentrations of Lead and Chromium Compounds in the Supernate After Adsorption on Pristine Lignin (ppm)**

Time	Lead	Chromium
0 hr.	10	10
1 hr.	10	7.4
	10	7.4
2 hr.	10	6.3
	10	6.5
4 hr.	10	5.95
	10	5.95
8 hr.	10	6.3
	10	6.3
1 day	6.0	6.3
	--	5.95
2 day	7.0	6.6
	6.75	6.75
4 day (0.25g lignin)	6.75	5.6
4 day (0.5g lignin)	2.2	4.87
	3.7	5.0

Table 44 Questionable Test Results - Initial Size Study

Residual Concentrations (ppm) of the Model Compounds
After Adsorption on Lignin (4 days)

	Lignin	Aniline	Phenol	Iso-phorone	Naphtha-lene	Penta-chloro-phenol	Bis(2eth - ylhexyl phthalate	* 2, 4-D	Trichloro-ethylene	* Lead	* Chromium
C_0	Nominal	5 ppm	5 ppm	1.6	2.04	1.69ppm	3.7ppm	1.25ppm	3.7ppm	10 ppm	10 ppm
	Actual	5.112	1.924	1.088	1.382	1.546	1.294	1.381	0.3986	8	9.89
		5.052	1.714	1.099	1.356	1.423	1.248	1.329	0.3860	8	9.9
	Ethanol Extracted										
	30 X 40		2.459			BDL		0.770	0.4378	7.83	4.19
			3.332			BDL		0.757	0.2329	7.3	5.34
	40 X 60	0.1495	2.333	0.621	0.274	BDL	0.907	0.727	0.2871	7.37	4.55
		0.136	2.059	0.412	0.164	BDL	0.562	0.767	0.767	7.2	4.56
	60 X 100	2.56	2.474	0.866	0.331	BDL	0.315	0.254	1.0602	6.4	4.93
		3.622	2.476	0.514	0.303	BDL	0.251	0.770	0.6195	7.5	4.65
	NAOH Extracted										
	60 X 100	0.173	1.206	0.726	0.480	0.547	1.253	0.926	0.1639	5.5	0.86
		0.207	1.183	0.661	0.664	0.525	1.854	1.002	0.1131	7	0.92

* Valid results. All others were invalidated

Note: Sample volumes of 100 ml (except 120 ml for trichloroethylene) were employed

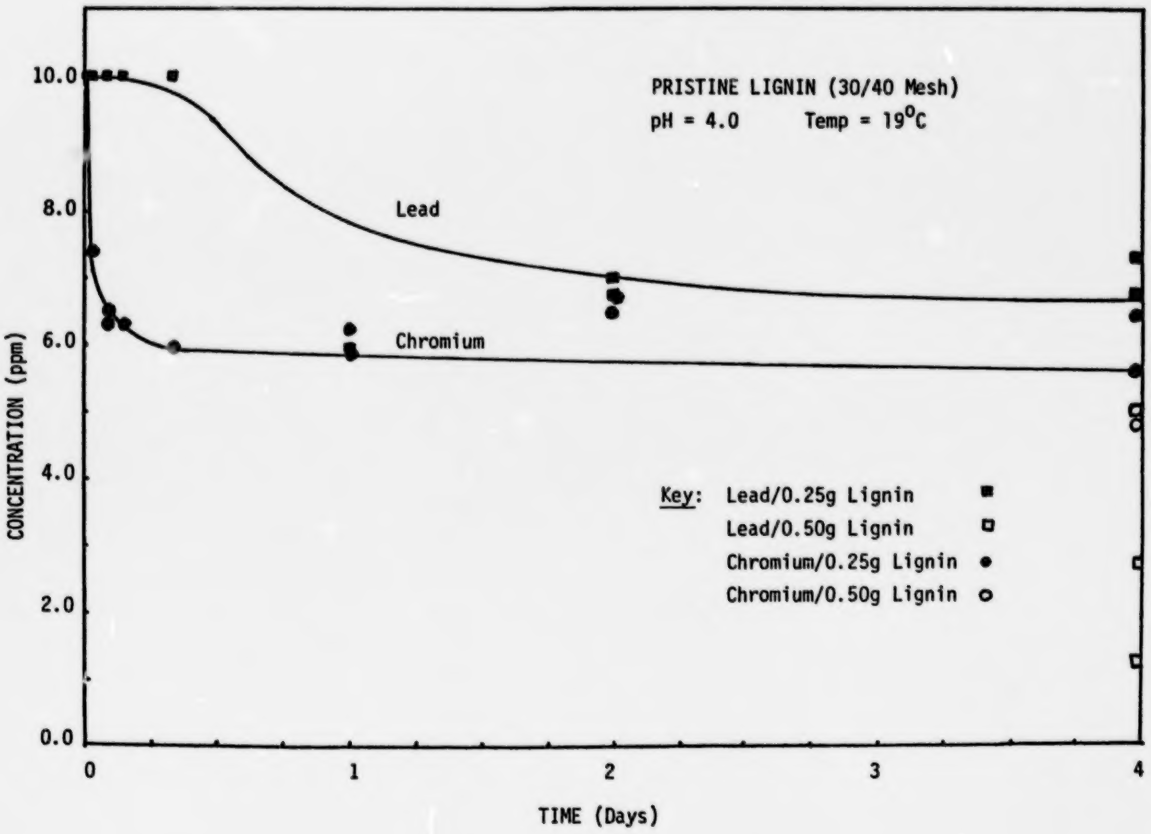


FIG. 46 KINETIC STUDY OF THE ADSORPTION OF HEAVY METALS ON PRISTINE LIGNIN (Cr and Pb)

of lead and chromium and of 2,4-D. The questionable tests were invalidated due to a malfunction of instrumental analysis equipment in our laboratories which delayed the analysis process for several days (the analyses were eventually performed on different instruments and with different programs). While trends could be observed, the scatter was too great to be reliable quantitatively. Undoubtedly, evaporative losses of organics accounted for a good deal of the scatter. Consequently, the study was repeated. However, the initial results are reproduced to cite the qualitative trends and for comparison to the rerun series.

The results of the rerun experiments were self-consistent as shown in Table 45 for the model organic compounds and in Table 46 for the organic compounds (for both runs).

The values for a cumulative "adsorptive capacity" of the lignin at each size range, for the organic compounds in the multicomponent solution based on the final, equilibrium concentration was calculated and are presented in Table 47. It may be noted that the ethanolic lignin had a "cumulative adsorptive capacity" value which was 36% greater than that of the comparable alkaline lignin (60 x 100 mesh). However, a review of Table 45 indicates that the alkaline isolate might be a stronger adsorbent for specific compounds, e.g., aniline and trichloroethylene. One major factor is that there is a significant difference in the surface area of these lignin isolates. The ethanolic lignin isolate had a measured surface area of 30 m^2/g as compared to 0.1 m^2/g for the alkaline isolate, suggesting that the alkaline lignin, if modified to increase its surface area, could potentially exceed the adsorption capacity of the ethanolic isolate. The fact that significantly higher yields of lignin are obtained by alkaline extraction further encourages

Table 45

Reliable Test Results - Second Size Study (Organics)

Concentrations (ppm) of Model Organic Compounds in the Supernatant
After Adsorption on the Pristine Lignin (250mg)
Equilibration Time: 4 days

Lignin	Aniline	Phenol	Isophorone	Naphthalene	Pentachlorophenol	Bis(EtHex) phthlate	Trichloroethylene
C_o							
Nominal	4.758	5.337	2.043	2.259	2.610	4.031	3.336
Actual	4.447	4.346	1.985	2.113	1.833	2.790	2.583
	4.130	4.298	2.002	1.856	2.123	3.500	2.604
ELOH							
Extract 30X40	3.130	4.346	1.467	0.660	0.360	1.263	2.058
	3.222	4.036	1.500	0.453	--	1.349	1.847
40X60	2.917	4.209	0.969	0.665	--	1.514	1.333
	2.164	4.357	1.003	0.654		1.143	1.398
60X100	1.577	3.340	1.434	0.428	--	0.774	1.577
	1.620	3.832	1.340	0.597	--	0.854	1.520
NAOH Extract 60X100	1.230	3.987	1.695	1.053	0.488	2.392	1.348
	1.420	4.099	1.587	0.857	0.665	2.184	1.477

Note: Sample volumes of 100 ml were used (except for trichloroethylene: 120 ml)

Table 46 Reliable Test Results - Initial and Second Size Studies

Adsorption of Lead and Chromium of Lignin (4 days)

Lignin	Lead	Lead (duplicate)	Chromium
C_0 Nominal	10 ppm	10 ppm	10 ppm
Actual	8	11.30	9.89
	8	11.02	9.9
Ethanol extracted			
30 X 40	7.83	7.50	4.19
	7.3	8.00	5.34
40 X 60	7.37	6.5	4.55
	7.2	8.50	4.56
60 X 100	6.4	6.50	4.93
	7.5	6.45	4.65
NaOH extracted			
60 X 100	5.5	2.50	0.86
	7	2.00	0.92

Table 47

Cumulative Adsorption Capacity of Lignin Types and Sizes for a 7-Component Organic Mixture

Lignin Type	Mesh Size	Sieve Opening (mm)	Adsorption Capacity (g/kg)
EtOH-Lignin **	30x40	0.59 - 0.42	3.66
	40x60	0.42 - 0.25	4.43
	60x100	0.25 - 0.15	5.30
NaOH-Lignin *	60X100	0.25 - 0.15	3.90

* "Cumulative Adsorption Capacity: based on the sum of the final, equilibrium concentrations for the seven model organic compounds

** The surface area of the ethanolic isolate (30x40 mesh) is 30sq. m/g. A comparable alkaline lignin isolate (30x40 mesh) is 0.1 sq. m/g.

the preferential selection of alkaline lignins for development as an adsorbent.

Since the surface of spherical particles (A) is a second-power function of the radius (r) or the diameter (d),

$$A \quad (\text{sphere}) \quad = \pi d^2 \quad = \quad 4 \quad \pi \quad r^2$$

and assuming that a sphere is a reasonable approximation of the geometry of the lignin particles, and since a 30 x 40 mesh fraction has an average diameter (50.5mm) which is more than twice that of a 60 x 100 mesh fraction (20mm), one might expect at least a four-fold increase in adsorption capacity due to surface adsorption effects alone.

The comparatively modest increases in absolute values of the "cumulative adsorption capacity" (Table 47) for the seven model organic compounds due to use of smaller particle size fractions strongly suggests that the mechanism of adsorption is confined to surface adsorption sites which are probably saturated relatively quickly and, additionally, are only partially bonded, i.e. only a fraction of adsorption sites are being used, perhaps due to steric hindrance arising from a rapid build-up (deposition) of adsorbed layers.

The results of the adsorptive studies for chromium and lead (Table 46) suggest that the alkaline isolate possesses a significantly higher adsorption capacity for heavy metals than does the lignin isolated by ethanol extraction.

For the duplicate lead run, an adsorption capacity value of 1.88 g/kg was calculated for the 60 x 100 mesh ethanolic lignin isolate at its equilibrium concentration and an adsorption capacity value of 3.56 g/kg for the alkaline lignin isolate (60 x

100 mesh). The corresponding values for the chromium determination are 2.04 g/kg for the ethanolic lignin and 3.60g/kg for the alkaline isolate (Table 48).

If one defines the adsorption ability of a resin by the percentage of metal ions adsorbed based on the concentration of the original solution (13), the values for alkaline lignin are significant (Table 48): for lead, 80% and for chromium 91%.

The difference in behavior of ethanolic isolates and alkaline isolates may be due in part to the ionization of organic acid functional groups in the lignin macromolecular structure, as a consequence of the alkaline hydroxide extraction. Thus, phenolate and carboxylate anions are likely to be present in greater concentration in the alkaline lignin isolates, introducing a net increase in the contribution to the adsorption process as a result of ion-exchange processes between heavy metal cations and residual sodium ions. On the other hand, the acidic conditions (pH = 3-5), typically employed during the adsorption studies, would be expected to depress the dissociation of phenolic hydroxyl and carboxylic acid groups in the ethanolic lignin isolates, thus minimizing cationic exchange and/or complexation of heavy metal ions.

Activated Carbon Adsorption Isotherms

The practical application of an adsorbent requires a knowledge of what compounds are adsorbable and at what loading. With the increasing application of activated carbon for the adsorption of toxic compounds, a need arose to establish a data base and experimental techniques which would allow reliable comparison of the adsorbability among compounds on activated carbon. A major report (14) which described carbon adsorption

Table 48

Adsorption Capacity and Ability of Lignin Isolates for Heavy Metal Ions

Lignin	Ion	Adsorption Capacity @ Equilibrium Concentration (g/kg)	Adsorption Ability * (% Ion Adsorbed)
Alkaline	Chromium	3.60	91
(60x100 mesh)	Lead	3.56	80
Ethanolic	Chromium	2.04	52
(60x100 mesh)	Lead	1.88	42

* Percentage of metal ions adsorbed based on original concentration (C_0); $C_o = 10$ ppm

isotherms for toxic organics was published in 1978 by the U.S. Environmental Protection Agency. A result of that study was to standardize the experimental procedure, as well as the method of reporting adsorption data, so that all information on adsorption was accomplished on a comparable basis. With some modification, the USEPA procedure, which describes adsorption by batch equilibrium carbon adsorption isotherms with results plotted according to the Freundlich adsorption equation, was adopted. The USEPA study used Calgon Filtrasorb 300 granular activated carbon (200 x 400 mesh) whereas Calgon Filtrasorb 400 (30 x 40 mesh) was used in this study in order to facilitate comparison with the lignin isolates and deionized water was used rather than a "mineralized" distilled water or simply distilled water as employed in the USEPA study. Furthermore, a pH of 3.5 ± 1 was used in this study (since pristine lignin will be employed in a non-alkaline medium) rather than a pH of 7.4 (although the USEPA researchers adjusted their pH, when necessary, with dilute solutions of sodium hydroxide or sulfuric acid).

The treatment and presentation of data followed the procedure described, as follows, by the USEPA investigators:

TREATMENT OF DATA

The carbon adsorption data were plotted according to the Freundlich equation. While this equation is empirical it is nonetheless widely used and has been found to describe adequately the adsorption process in dilute solution. The Freundlich equation has the form:

$$\frac{X}{M} = KC_f^{1/n} \tag{1}$$

The data were fitted to the logarithmic form of the above equation, which has the form:

$$\log \frac{X}{M} = \log K + 1/n \log C_f \tag{2}$$

where:

$X = C_o - C_f$ = initial concentration of solute in mg/l minus final concentration in solution at equilibrium
M = weight in grams of adsorbent (carbon)
C_f = final concentration of solute in mg/l at equilibrium
K = intercept at $C_f = 1$ ($\log C_f = 0$)
1/n = slope of the line

For the dilute solutions in this study, this equation yields a straight line with a slope of 1/n and an intercept equal to the value of K when $C_f = 1$ ($\log C_f = 0$). The intercept is roughly an indicator of adsorption capacity and the slope, 1/n, of adsorption intensity. The concentration of compound on the carbon in equilibrium with a concentration C_f is given by the X/M value, expressed as mg compound/gram of carbon.

PRESENTATION OF DATA

The experimental data for each of the compounds are shown in data sheets. Carbon dosages are shown on the left along with the initial concentration, C_o, and residual concentrations after treatment with carbon. These values were then used to calculate the amount of compound removed (C_o-C_f) and the carbon loading, X/M. Some of the compounds were tested at differing pH's. The data were then plotted according to equation (2) on log-log coordinates. Linear least squares regression analysis was used to locate the line. When pH had no observable effect on adsorption, all of the data points were plotted and represented by a single line. Where pH affected adsorption, individual lines were drawn to show the effect of pH.

On the second data page for each compound, the molecular structure, formula and molecular weight of the compound are given. The equation of the regression line was then used to calculate the values for the intercept, K, and the slope 1/n. The K value, therefore, represents the carbon loading, X/M, in mg compound/gram of carbon at equilibrium with 1 mg compound/liter. Also shown is the correlation coefficient, r.

As the Freundlich equation indicates, the loading on the carbon, X/M, is a function of the equilibrium concentration of compound. This effect is shown in the next table on a data sheet which gives adsorption capacity in mg/gram for varying initial concentrations of organic compound ranging from 0.1 to 10 mg/l. These values were calculated from the equation of the regression line. (See, for example, Figure 55, the USEPA Carbon adsorption isotherm for phenol).

The Freundlich equation can be rearranged to calculate the carbon dose required to reduce any initial concentration of compound to some predetermined residual concentration. If, for the term X, use is made of its equivalent, C_o-C_f, in which C_o equals the initial concentration of organic compound and C_f the residual concentration, the equation can now be written as follows:

$$\frac{Co-Cf}{M} = KC_{\substack{f\\f}}^{1/n} \qquad (3)$$

To determine carbon dose the equation can be rearranged to the logarithmic form:

$$\log(C_o-C_f) - \log M = \log K + 1/n \log C_f \qquad (4)$$

This equation is linear when M (carbon dose) is plotted against C_o (initial concentration) on ordinary coordinate paper. These calculations were made for a range of initial concentrations and a range of final concentrations. The resulting carbon doses in mg/l are tabulated. Where pH was varied, only the data for neutral pH was used. For compounds which were essentially non-adsorbable, the calculated carbon dosages were considered too high to be practical and are shown in the table as greater than 10,000 mg/l carbon. The tabulated carbon doses represent removals obtainable in a single-stage contactor. More efficient use of carbon can be realized by multiple stages of contacting. The carbon dose values are, however, useful for comparative purposes and to ascertain whether use of carbon is feasible for removal of the compound.

Data are provided to calculate the carbon dose to reduce any initial concentration of compound to any desired final concentration. For example, consider the following for benzidine (where K = 220 and 1/n = 0.37). To calculate the carbon required to reduce a benzidine concentration from 10 mg/l to 0.1 mg/l in neutral solution, equation (4) is used and the values for the constants are taken from the table of constants for benzidine. Thus

$$\log(10-0.1) - \log M = \log 220 + 0.37 \log 0.1$$
$$M = 100 \text{ mg/l of carbon}$$

The tabulated carbon doses are also useful to illustrate the benefit of more than one stage of treatment. Consider again the case of benzidine. To reduce an initial concentration of 10 mg/l to 0.1 mg/l in a single stage requires 100 mg/l of carbon. If removal is accomplished in two stages, i.e., 10 mg/l to 1.0 mg/l in the first stage followed by 1.0 mg/l to 0.1 mg/l in a second stage, the carbon dose is 40 mg/l + 9.4 mg/l = 49.4 mg/l of carbon or about one-half the dose required in a single stage process.

"Part I" Results

Complete adsorption isotherm studies were performed with aniline, with 2-4-dichlorophenoxy acetic acid (2,4-D), and for chromium which were not available in the USEPA studies.

The results of the adsorption analysis of aniline at eight dose levels of activated carbon (in duplicate) are presented in Table 49. The Freundlich parameters calculated for aniline on activated carbon are presented in Table 50. An adsorption capacity (K) of 11.9 g/kg was found. The adsorption isotherm,

Table 49 Adsorption Isotherm Analysis: Aniline On Activated Carbon

Sample No.	Final Conc. (c_f) (ppm)	Carbon dose (m) (mg/100ml)	X/M (mg/g)
Initial Conc'n:			
Co(1)	9.66		
Co(2)	9.88		
Co(avg.)	9.77		
1	8.45	1.32	100
2	8.87	1.17	76.92
3	7.51	2.56	88.11
4	7.23	2.62	96.95
5	6.73	5.05	60.2
6	6.04	5.36	69.59
7	4.59	10.47	49.47
8	4.92	10.41	46.59
9	2.27	24.85	30.20
10	2.80	25.79	26.99
11	0.21	49.93	19.15
12	0.54	51.48	17.95
13	BDL	100.52	--
14	0.01	101.30	9.76
15	BDL	201.10	--
16	BDL	201.19	--

Notes:

(a) $X = Co - C_f$

(b) BDL = Below detectable limits

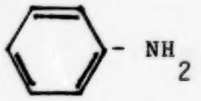
(c) pH = 5.0 ± 0.5°C; T = 23.5 ± 1°C

(d) Calgon Filtrasorb 400

Table 50 Freundlich Parameters: Aniline on Activated Carbon

Compound: Aniline

Structure:



Formula: C6H5N

Molecular Weight: 93.3

Freundlich Parameters*

K = 11.9

1/n = 0.95

Correlation Coefficient (r) = 0.9347

*pH = 5.0; Initial concentration (C_o) = 9.77 mg/l obtained by linear regression analysis (r = 0.9503), for aniline on activated carbon (pH = 5.0 ± 0.5; T = 23.5 ± 1.0°C: C_o = 9.77 ppm) is given in Figure 47.

The results of the adsorption analysis for 2,4-dichlorophenoxy acetic acid (2,4-D) are presented in Table 51. Unfortunately, the compound was rapidly adsorbed at the carbon dose levels chosen for the study and its concentration went below detectable levels using electron capture detection with the gas chromatograph.

A nominal adsorption isotherm based on the two (average of four) results is presented in Figure 48. The K value is approximately 8.2, corresponding to a roughly estimated adsorption capacity of 8.2 mg/g carbon for "2.4-D" at an initial concentration 2.5 mg/l and pH = 4.2.

The results of the adsorption analysis for chromium on activated carbon is presented in Table 52. The Freundlich parameters calculated for chromium on activated carbon are presented in Table 53. An adsorption capacity (K) of 8.96 g chromium adsorbed/g Carbon is estimated under the experimental conditions. The adsorption isotherm, obtained by linear regression analysis (r = 0.9522), for chromium on activated carbon is given in Figure 49.

Table 51 Adsorption Isotherm Analysis: 2,4-D on Activated Carbon

Sample No.	Final Conc'n. (C_f), ppm	Carbon Dose (M) mg/100 ml	X/M*, mg/g
Initial Conc'n.			
C_o (1)	2.475		
C_o (2)	2.432		
C_o (Avg)	2.453		
1	0.238	1.00	221.5
2	0.269	1.19	183.5
3	0.12	2.54	96.10
4	0.199	2.66	91.47
5	BDL		
6	BDL		
.	.		
.	.		
.	.		
.	.		
.	.		
16	BDL		

Notes: a) X/M $= C_o - C_f$

b) BDL = Below detectable limits

c) pH = 4.2; T = 23.5 ± 1 °C

d) Calgon Filtrasorb 400

Table 52 Adsorption Isotherm Analysis: Chromium on Activated Carbon

Sample No.	Final Conc'n. (C_f), ppm	Carbon Dose (M) mg/100 ml	X/M*, mg/g
Initial Conc'n.			
C_o (1)	8.99		
C_o (2)	9.43		
C_o (Avg)	9.21		
1	5.56	5.15	70.854
2	5.295	5.75	68.087
3	3.027	13.18	46.912
4	3.856	11.55	46.355
5	2.123	25.96	27.300
6	2.139	25.00	28.284
7	1.371	50.24	15.54
8	1.20	50.45	15.72
9	1.245	100.00	7.965
10	1.21	100.56	7.955
11	2.186	150.51	4.667
12	1.932	149.88	4.856
13	1.598	200.74	3.792
14	1.840	200.45	3.677
15	1.515	251.30	3.062
16	1.801	250.79	2.954

Notes: a) $X/M = C_o - C_f$

b) pH = 4.1 ± 0.05; T = 23.5 ± 1 °C

c) Calgon Filtrasorb 400

Table 53 Freundlich Parameters: Chromium on Activated Carbon

Freundlich Parameters*	
K	= 8.96
1/n	= 1.275
Correlation Coefficient (r)	= 0.9522

*pH = 4.1; Initial concentration (C_o) = 9.21 mg/l

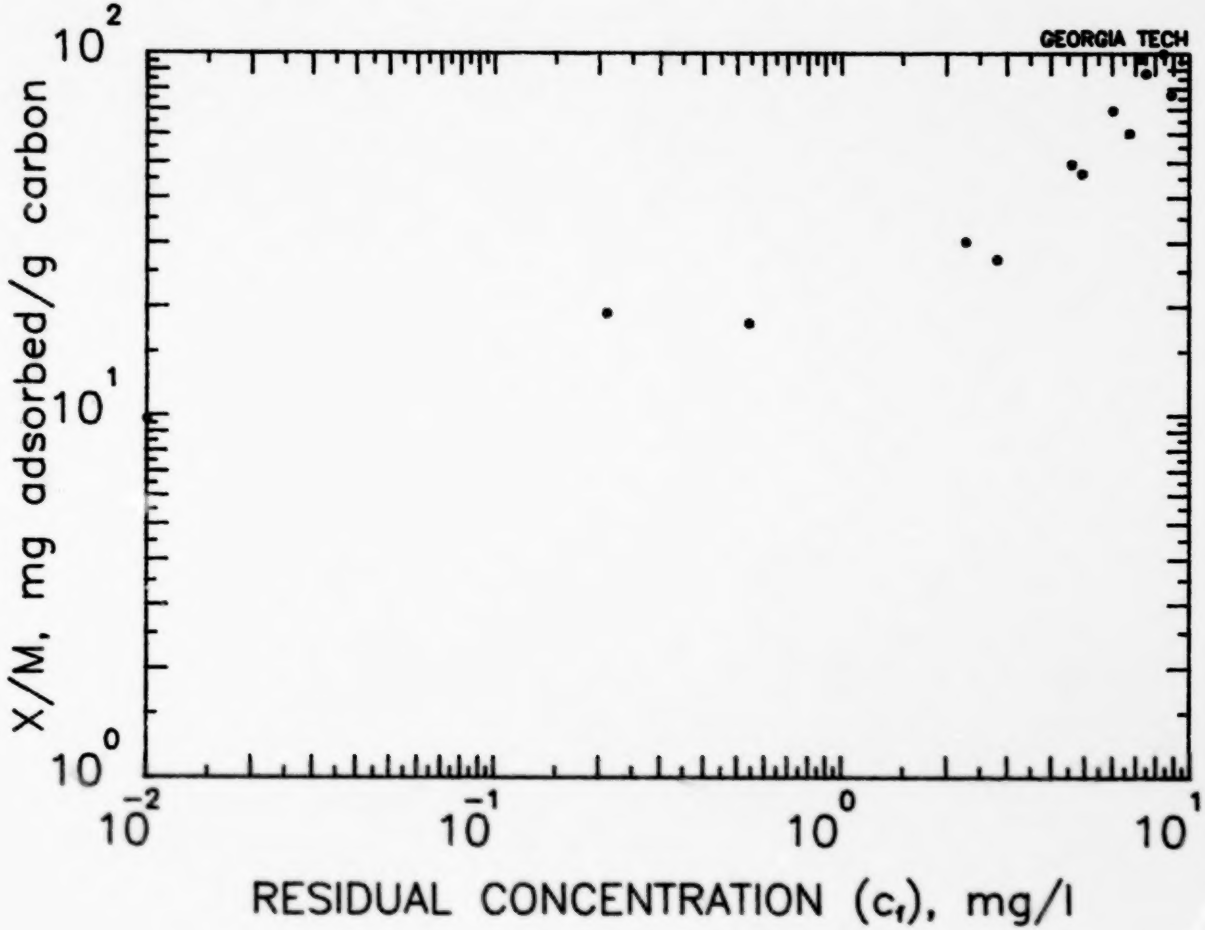


Figure 47 Carbon Adsorption Isotherm–Aniline

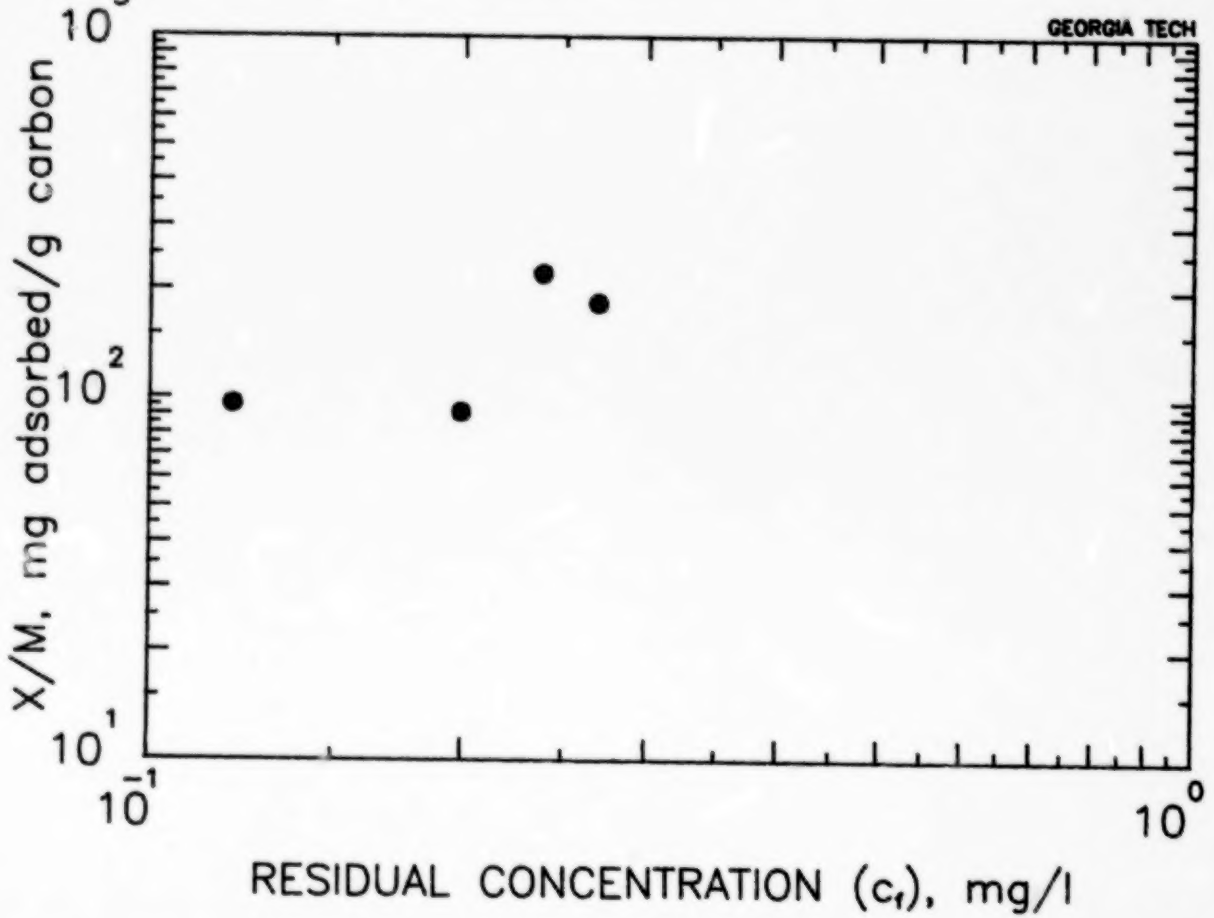


Figure 48 Carbon Adsorption Isotherm–2,4 D.

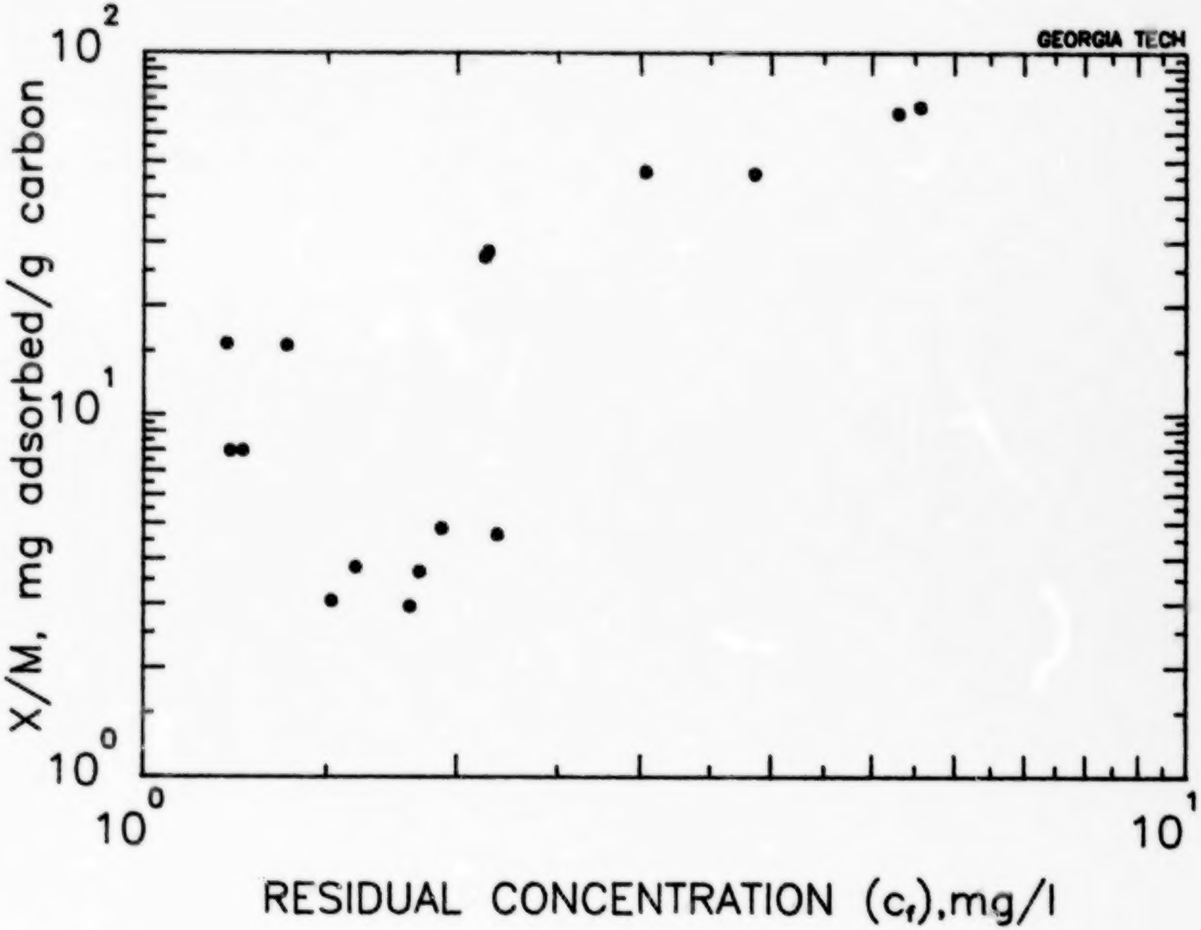


Figure 49 Carbon Adsorption Isotherm–Chromium.

The adsorption behavior of chromium at the highest carbon dose level showed an anomalous increase in the residual concentration which may be attributable to an attrition of the porous structure of the activated carbon particles due to the continuous vigorous shaking during the experiment. The resultant breakdown in the solid was evident during centrifugation when the supernate could not be clearly separated from the finely dispersed carbon particles. The net effect may have been to reduce the effective (available) carbon dose for adsorption.

The linear dependence of the adsorption isotherms and reasonable correlation coefficients indicate that the experimental procedures are sound and that the data are reliable.

"Part II" Results

Adsorption isotherms and Freundlich parameters for the following organic compounds were available from the USEPA report (14):

- Phenol
- Pentachlorophenol
- Isophorone
- Naphthalene
- Bis (2-ethylhexyl) phthalate
- Trichloroethylene

Single point data was generated in our laboratories under conditions similar to, but not exactly the same as, those reported by the USEPA. The results of this study are compared with the USEPA data in Table 54. With the notable exception of the result for bis(2-ethylhexyl) phthalate there is generally very good agreement considering differences in (a) pH, (b) particle size, and (c) the grade of activated carbon, as discussed earlier. The adsorption capacity value (K) of 11,300, reported by USEPA for the phthalate, appears to be

Table 54 Comparison of GIT Experimental Data for Selected Model Compounds with USEPA Carbon Adsorption Isotherms and Freundlich Parameters

Compound	GIT Experimental Results					USEPA Data (b)			
	Carbon: Calgon Filtrasorb 400 Size: 30 x 40 Mesh					Carbon: Calgon Filtrasorb 300 Size: 200 x 400 Mesh			
	pH	C_o (ppm)	C_f (ppm)	M (mg/L)	X/M (mg/g)	pH	C_o (ppm)	C_f (ppm)	X/M (mg/g)
Phenol (a)	3.98	11.03	1.545 1.856	204.8 212.3	44.68 44.79	3.0	10.	1.54 1.85	52. 65.
Pentachlorophenol	3.80	7.76	BDL(b) BDL	66.9 73.2	(116)	3.0	10. 1.		630. 260.
Isophorone	3.90	1.31	0.648 0.866	25.5 25.3	26. 17.55	5.5	1.	0.65 0.86	25. 28.
Naphthalene	3.97	8.545	0.313 0.404	62.5 73.9	131.7 110.1	5.6	8.07	0.30 0.40	80. 90.
Bis (2-ethylhexyl) phthalate	3.96	13.62	5.05	35.7	240.0	5.3	1.0		11.300(c)
n-butyl phthalate									220. (c)
Trichloroethylene	4.0	0.932	0.031 0.034	120.0 120.0	7.51 7.48		1.0	0.0324	3.34

Notes: (a) Phenol data for USEPA is pooled
(b) BDL = Below detectable limits
(c) Value of 11,300 questionable: Result for n-butyl phthalate believed to be more accurate for phthalate compounds

extraordinarily high for an organic compound. In fact, in the summary of Freundlich parameters at neutral pH of that report the highest reported value is 360 mg/g, suggesting strongly that the result of 11,300 is highly questionable. Furthermore, and more in keeping with comparability to our experimental results (240 and 274), the USEPA summary reports a value of 220 mg/g for n-butylphthalate which is functionally similar to the bis(2-ethylhexyl) phthalate.

Based on the results of Parts I and II, it was concluded that the experimental methodology being employed in this study was reliable and that the analytical methods would be valid for evaluation of lignin adsorption isotherms.

Adsorption Isotherms: Pristine Lignin

Adsorption isotherms representative of four groups of hazardous waste compounds on alkali-isolated pristine lignin were determined. The compounds are representative of acid-and neutral - extractables (phenol, naphthalene), pesticides (2,4-dichlorophenoxy acetic acid), purgeables (trichloroethylene) and heavy metals (chromium).

The experimental data for each of the model compounds are tabulated and the corresponding adsorption isotherms for both pristine lignin and activated carbon produced by application of the Freundlich equation, are presented in accordance with the following schedule:

Phenol	Table 55;	Figure 50
Naphthalene	Table 56;	Figure 51
2,4-D	Table 57;	Figure 52
Trichloroethylene	Table 58;	Figure 53
Chromium	Table 59;	Figure 54

Table 55 Adsorption Isotherm Analysis: Phenol on Pristine Lignin

Sample	Final Conc'n, C_f (ppm)	Adsorbent Dose, M (mg/100 ml)	X/M, (mg/g)
Initial Concentration			
C_o (1)	9.80		
C_o (2)	10.02		
C_o (Avg)	9.91		
1	7.75	10.4	20.77
2	7.69	11.2	19.82
3	7.33	26.9	9.591
4	7.3	25.7	10.156
5	6.82	51.0	6.059
6	6.8	50.9	6.110
7	6.0	100.5	3.891
8	6.15	101.2	3.715
9	5.7	199.5	2.065
10	5.40	200.1	2.254
11	5.34	301.0	1.518
	5.12		
12	4.9	300.4	1.668
13	4.08	400.2	1.457
14	4.52	404.4	1.333
15	3.53	500.6	1.274
16	3.4	500.3	1.301

(1) Regression Analysis:

$r = 0.8932$	$k = 0.0127$
$a = -1.896$	$n = 0.305$
$b = 3.274$	

(2) $X = C_o - C_f$

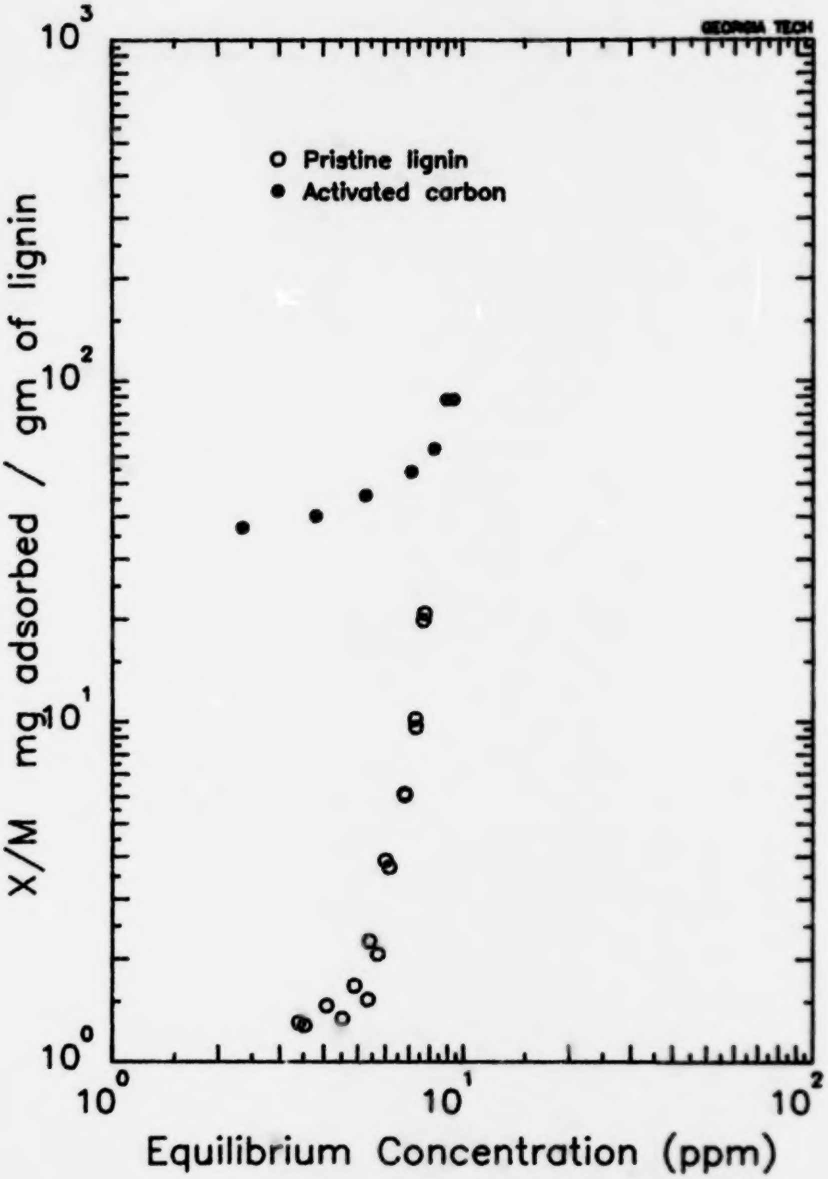


Figure 50 Adsorption isotherm of phenol for activated carbon and pristine lignin

Table 56 Adsorption Isotherm Analysis: Naphthalene on Pristine Lignin

Sample	Final Conc'n, C_f (ppm)	Adsorbent Dose, M (mg/100 ml)	X/M, (mg/g)
Initial Concentration			
C_o (1)	7.52		
C_o (2)	8.54		
C_o (Avg)	8.13		
1	7.63	10.0	5.00
2	7.54	10.0	5.90
3	7.4	25.6	2.852
4	6.81	26.6	4.962
5	7.94	50.5	0.376
6	6.12	51.3	3.918
7	5.52	100.8	2.589
8	5.05	102.4	3.008
9	3.99	199.8	2.072
10	4.27	199.8	1.932
11	3.58	300.6	1.514
12	3.30	301.6	1.601
13	2.41	401.0	1.426
14	1.90	401.6	1.551
15	0.97	500.3	1.431
16	1.09	499.9	1.408

(1) Regression Analysis:

r = 0.821 k = 1.051
a = 0.0217 n = 1.603
b = 0.624

(2) $X = C_o - C_f$

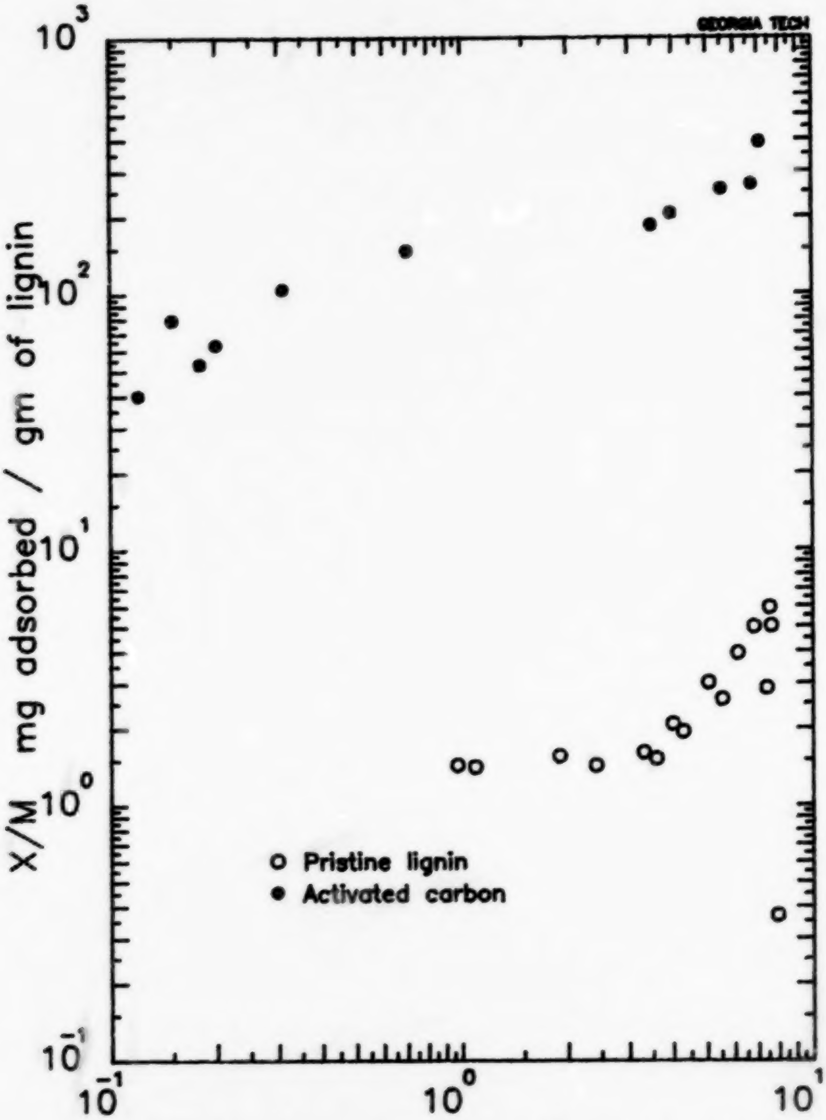


Figure 51 Adsorption isotherm of naphthalene for activated carbon and pristine lignin

Table 57 Adsorption Isotherm Analysis:
"2,4-D" on Pristine Lignin

Sample	Final Conc'n, C_f (ppm)	Adsorbent Dose, M (mg/100 ml)	X/M, (mg/g)
Initial Concentration	2.70		
1	2.40	1.16	25.862
2	2.53	1.26	13.49
3	2.28	2.86	14.685
4	2.31	2.45	15.918
5	2.16	4.87	11.088
6	2.10	5.07	11.834
7	2.25	10.3	4.369
8	2.09	0.98	6.112
9	1.57	19.8	5.707
10	1.48	20.4	5.980
11	1.3	31.4	4.459
12	1.35	30.7	4.397
13	1.109	40.9	3.890
14	1.158	41.3	3.734
15	1.04	50.0	3.320

(1) X/M = $C_o - C_f$

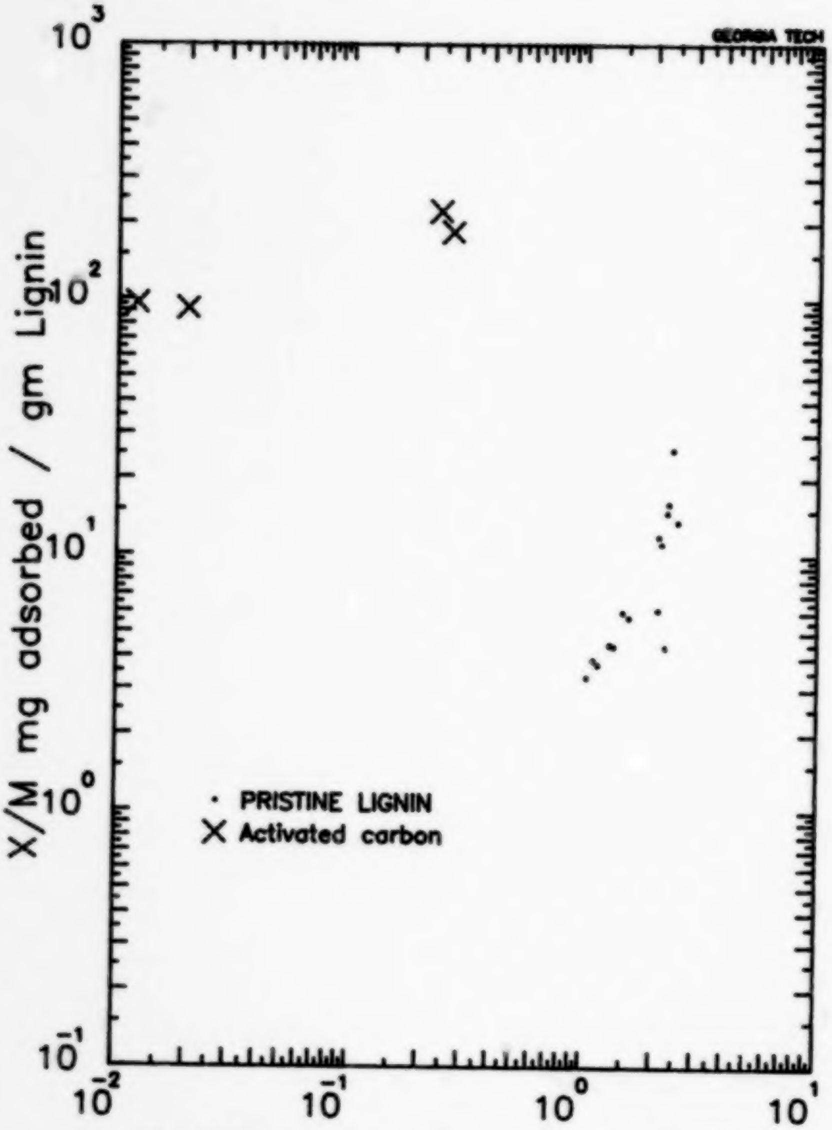


Figure 52 Adsorption isotherm of 2,4 – D for activated carbon and pristine lignin

Table 58 Adsorption Isotherm Analysis: Trichloroethylene on Pristine Lignin

Sample	Final Conc'n, C_f (ppm)	Adsorbent Dose, M (mg/100 ml)	X/M, (mg/g)
Initial Concentration C_o	2.29		
1	1.240	250.6	0.419
2	1.200	253.6	0.430
3	1.360	200.0	0.465
4	1.320	200.8	0.483
5	1.430	150.2	0.572
6	1.400	151.3	0.588
7	1.509	100.7	0.776
8	1.714	101.1	0.570
9	1.614	50.3	1.344
10	1.714	50.6	1.138
11	1.872	25.5	1.639
12	1.793	26.7	1.861
13	1.970	10.8	2.963
14	1.810	11.4	4.211
15	2.019	5.47	4.954
16	2.085	5.49	3.734

(1) $X/M = C_o - C_f$

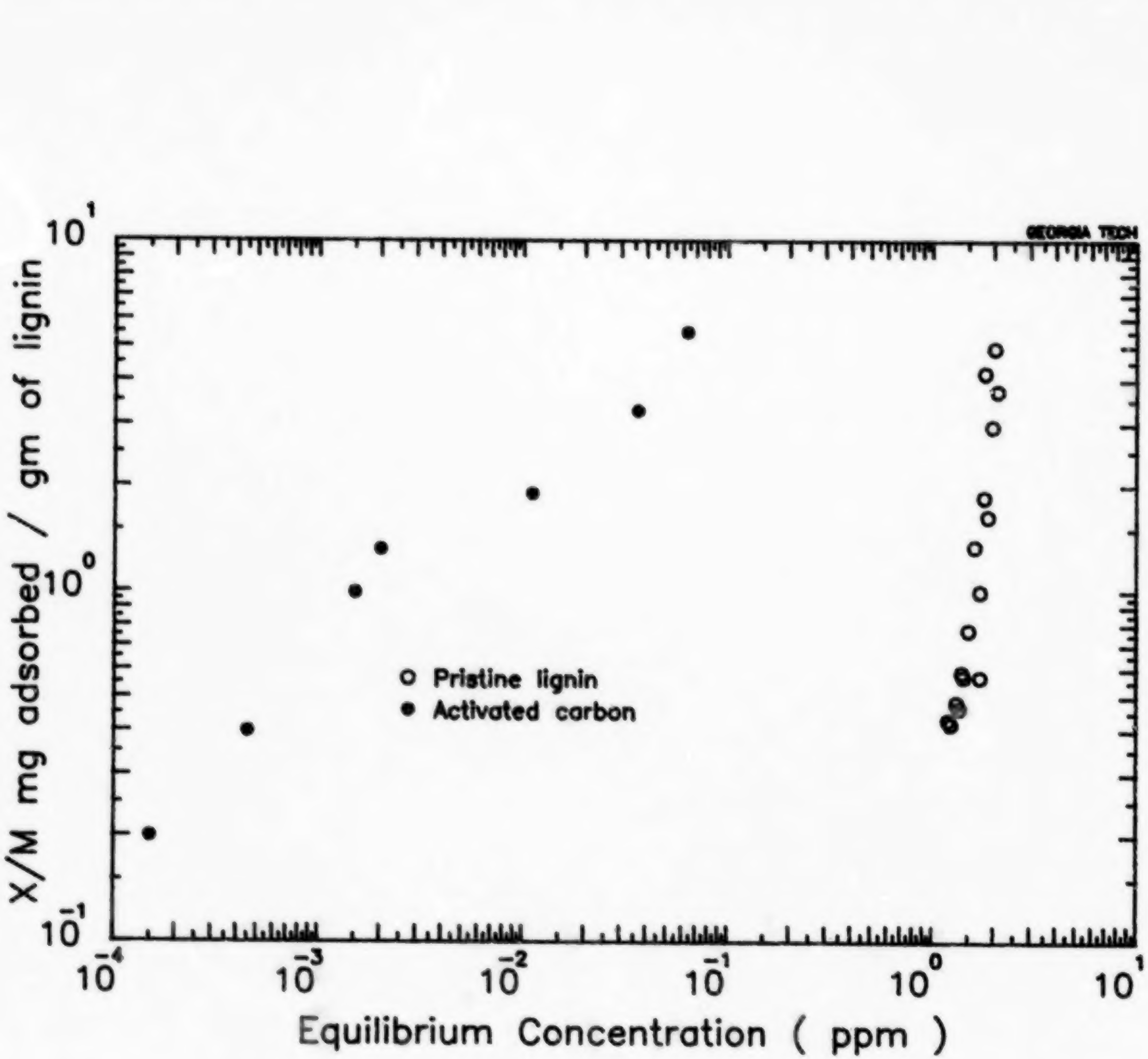


Figure 53 Adsorption isotherm of trichloroethylene for activated carbon and pristine lignin

Table 59 Adsorption Isotherm Analysis: Chromium on Pristine Lignin

Sample	Final Conc'n, C_f (ppm)	Adsorbent Dose, M (mg/100 ml)	X/M, (mg/g)
Initial Concentration C_o (Avg)	10.12		
1	8.77	5.08	26.57
2	9.89	0.86	4.73
3	8.17	11.4	17.10
4	8.04	10.5	19.81
5	6.12	28.2	14.18
6	7.33	25.1	11.12
7	3.50	50.5	13.11
8	4.04	50.7	11.99
9	2.02	100.6	8.05
10	1.91	100.3	8.29
11	1.84	150.3	5.51
12	1.62	151.5	5.61
13	1.73	200.5	4.18
14	1.66	200.7	4.22
15	1.015	250.2	3.64
16	1.069	251.3	3.62

Notes: (1) 89.7% of Initial Chromium Ions Adsorbed

(2) $X/M = C_o - C_f$

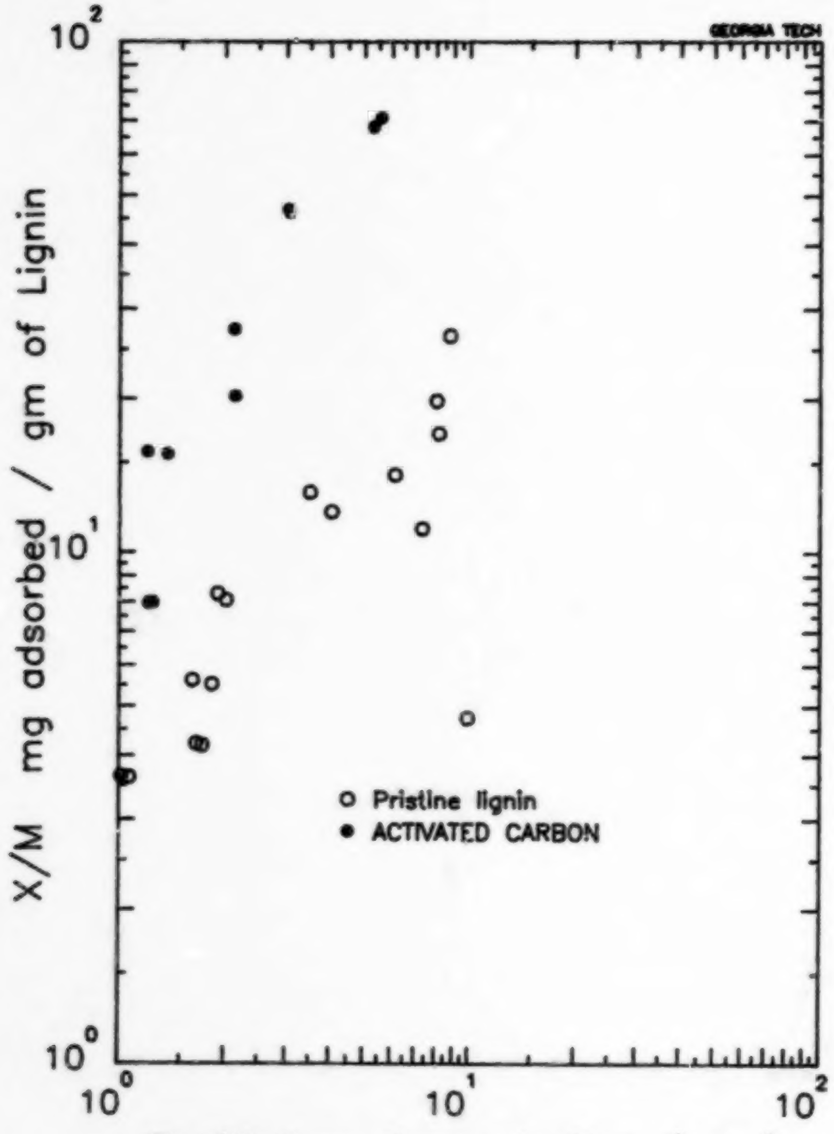


Figure 54 Adsorption isotherm of chromium for activated carbon and pristine lignin

Comparative analyses of the adsorption of phenol, of naphthalene, and of chromium on pristine (alkaline) lignin and activated carbon was possible.

The comparisons are based on Freundlich parameters selected from the adsorption isotherms of the given model compound at on arbitrary, but common, equilibration value.

In the case of phenol, a comparative analysis (Table 60) is made based on the USEPA adsorption isotherm for activated carbon (Figure 55, see also Table 55 of this report) and of the lignin isotherm (Figure 50). For purposes of the comparison, an equilibrium concentration value of 5.27 mg/l (ppm) reported in the USEPA data (Figure 55) was selected for the activated carbon adsorption study which was conducted under pH conditions (=3) similar to the lignin study. As can be seen in the Table accompanying Figure 55, that value of equilibrium concentration also corresponded to an initial phenol concentration (10 ppm) which is very close to that used for this study's lignin evaluation. The relative adsorptive capacity (X/M) of activated carbon for phenol under these conditions was reported to be 46 g/kg. These conditions also were defined by an adsorbent (carbon) dose of 100 mg/l. To make a relative comparison of the adsorbent properties of pristine lignin for phenol, an approximately equal equilibrium concentration value (C_f = 5.12 mg/l) was selected from the adsorption isotherm analysis for phenol on lignin (Table 55 and Figure 50). One notes that the corresponding adsorption capacity value is 1.6 g/kg and that the corresponding adsorbent dose is 3000 mg/liter.

A similar comparative analysis was made in the case of naphthalene (Table 61). The USEPA adsorption isotherm data for naphthalene on activated charcoal at pH = 5.6 (Table 62) and an

Table 60

Comparison of Adsorption Isotherms -- Phenol

Freundlich Parameters	Activated Carbon	Pristine Lignin
K	2.1	0.0127
1/n	0.54	3.274
corr. coef. (r)	0.89	0.8932
Initial conc. (ppm)	9.84	9.91
C_f (eq. conc.) (ppm)	5.27	5.12
Adsorption Capacity (mg/g)	46.	1.59
Adsorbent dose	100 mg/l	3000 mg/l

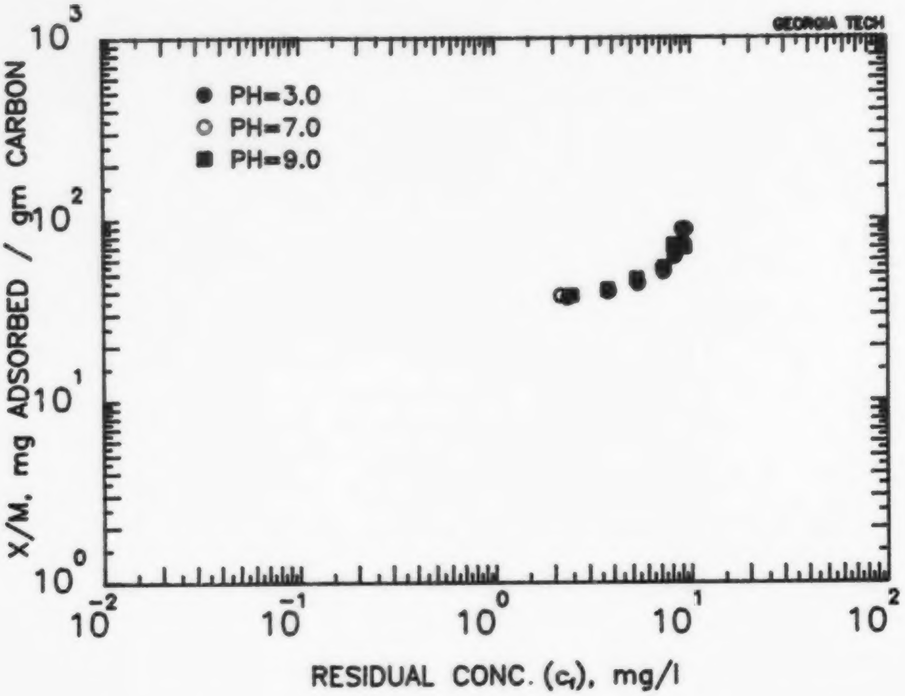


FIGURE 55. USEPA CARBON ADSORPTION ISOTHERM: PHENOL

	pH=3.0			pH=7.0			pH=9.0		
Carbon Dose mg/l	Cf	Co-Cf=X	X/M	Cf	Co-Cf=X	X/M	Cf	Co-Cf=X	X/M
0	9.84			9.80			9.96		
5	9.40	0.44	88	9.36	0.44	88			
10	8.96	0.88	88	9.06	0.74	74	9.26	0.70	70
25	8.27	1.57	63	8.24	1.56	62	8.17	1.79	72
50	7.12	2.72	54	7.24	2.56	51	7.26	2.70	54
100	5.27	4.57	46	5.36	4.44	44	5.27	4.69	47
150	3.80	6.04	40	3.74	6.06	40	3.75	6.21	41
200	2.35	7.49	37	2.15	7.65	38	2.45	7.51	38

Table 61

Comparison of Adsorption Isotherms of Naphthalene for Activated Carbon and Pristine Lignin

Freundlich Parameters	Activated Carbon (pH = 5.6)	Pristine Lignin (pH = 3)
K	132	0.2837
1/n	0.42	1.387
corr. coef. (r)	0.96	0.9077
Initial conc. (ppm)	8.07	8.13
C_f (eq. conc.) (ppm)	3.48	3.44
X/M (mg/g)	184	1.55
Adsorbent dose (M)	25 mg/l	3000 mg/l

Table 62 USEPA Adsorption Isotherm Data for Naphthalene on Activated Carbon

Freundlich Parameter	(pH = 5.6)
K	132
1/n	0.42
Corr. Coef (r)	0.96

Initial Conc.	Adsorption Capacity (X/M) mg/g
1.0 (ppm)	132
0.1	50
0.01	.9
0.001	7.3

Carbon dose (mg/l)	C_f (ppm)	$C_o - C_f = X$	X/M (mg/g)
0	8.07		
2.5	7.10	0.970	388
5.	6.74	1.33	266
10.	5.52	2.55	255
20.	3.97	4.10	205
25.	3.48	4.59	184
50.	0.70	7.37	147
75.	0.31	7.76	104
100.	0.15	7.92	79
125.	0.20	7.87	63
150.	0.18	7.89	53
200.	0.12	7.95	40

initial concentration of 8 ppm was used. The relative adsorption capacities for naphthalene were 184 g/kg and 1.6 g/kg for activated carbon and pristine lignin, respectively. To achieve the same (3.44 - 3.48 mg/l) equilibrium concentration an adsorbent dose of 25 mg/l of activated carbon or 3000 mg/l of pristine lignin was required.

For the case of heavy metals, pristine lignin appears to have significantly more potential as an adsorbent vis-a-vis activated carbon. For essentially similar experimental conditions (Table 63), the relative adsorption capacity is 8.7 g/kg for pristine lignin vs. 27.8 g/kg for activated carbon (see also Tables 52 and 53). The adsorbent doses required to achieve a similar residual concentration (2 mg/l) was 1.0 g/l for lignin vs. 0.25 g/l for activated carbon.

Reliable comparative analyses of trichloroethylene were not possible. Quite obviously (Table 58) and (Figure 53), pristine lignin is an ineffective adsorbent for trichloroethylene. In addition, the equilibrium concentration is only slightly affected by the adsorbent dose, suggesting that only a very minor adsorption process occurs on lignin.

With 2,4-D, the paucity of data for adsorption on activated carbon (Table 51, Figure 48, and Figure 52) and the dissimilar equilibrium (residual) concentration ranges achieved in the respective experimental series for carbon and lignin (Figure 52) precludes a comparative analysis. Qualitatively, however, it is obvious that pristine lignin has a much lower adsorption capacity than does activated carbon.

The surface area disparity between activated carbon (1000 m^2/g) and alkaline pristine lignin (0.1 m^2/g) undoubtedly

Table 63

Comparison of Adsorption Isotherms of Chromium for Activated Carbon and Pristine Lignin

Freundlich Parameters	Activated Carbon (pH = 3)	Pristine Lignin (pH = 3)
K	8.96	3.76
1/n	1.28	0.77
corr. coef. (r)	0.9522	0.907
Initial conc. (ppm)	8.99	10.12
C_f (eq. conc.) (ppm)	2.13	1.97
X/M (mg/g)	27.8	8.7
M (mg/1)	250.	1000.

contributes to the significantly different adsorptivities of the organic model compounds on the two adsorbents. The seemingly preferred affinity of phenol and chromium ions (and, to a lesser degree, naphthalene) among the model hazardous waste compounds, is indicative of a highly polar adsorption process at the surface of the lignin. The kinetics results indicate that heavy metal adsorption is probably due in large part to a cation exchange mechanism. In the case of phenol both hydrogen bonding (to phenolic hydroxyl and carboxylic acid groups) and quinonic-complexation mechanisms may be operable. Naphthalene's behavior may be attributed to π-electron delocalization and secondary bonding interaction with the aromatic nuclei of the lignin macromolecule. The poor results with 2,4-dichlorophenoxy acetic acid might not be obvious because of the carboxylic acid functional group. However, the bulk of the molecular volume of the compound is occupied by a dichlorophenyl ether moiety which could minimize occupation of surface adsorbent sites as well as the potential for multilayer sorption. Finally, as will be discussed further in the next section, little, if any, contribution is made to the adsorption processes by a porous microstructure which is characteristic of commercial adsorbents.

The shape of the isotherm curves of lignin is of the S-1 class per the Giles classification (15,16). The characteristic classes are based on the form of the initial part of the isotherm (S), and the subgroups relate to the behavior at higher concentration (1 in S-1). For the S class the initial slope is convex to the concentration axis, and this is frequently followed by a point of inflection leading to an S-shaped isotherm (the inflection was not observed in any of the lignin isotherms). The S isotherms are explained when the force of interaction between adsorbed molecules is significant relative to that between solute and adsorbent; the activation energy (for removal of the solute from the surface) will be higher (than that observed with L, or Langmuir, class systems where interaction between adsorbed molecules is negligible and the activation energy is independent of surface coverage). Cooperative adsorption occurs corresponding to an S isotherm. In these cases, the solute molecules tend to be packed in rows or clusters on the surface, and this situation is encouraged when the solvent (water) is strongly adsorbed, e.g., on a polar adsorbent (lignin) and the solute is monofunctional, as in the case of phenol. It has also been observed that S-shaped isotherms result for the adsorption of liquid solutes of limited solubility, the amount adsorbed increasing rapidly as the solubility limit is approached (17).

Adsorption Capacity of Steam Exploded Wood

Prior to the conclusion of this project and, in anticipation of the possibility that the limited surface area of alkaline-extracted lignin could yield marginal values of adsorption capacity, it was postulated that steam-exploded wood itself, through which the lignin was distributed (hopefully "homogeneously" in thin layers) on a presumably high-surface area fibrous structure, might have provided a solution to achieving a high-surface area lignin adsorbent composition.

Consequently, a sample of steam-exploded Tulip poplar was water-washed, dried, and screened through a 10-mesh screen and a preliminary evaluation of its utility as an adsorbent was undertaken with the seven-component organic solution, with 2,4-D, and with chromium and lead. Two dose levels were used and equilibration was terminated after four days. The results of the tests are shown in Tables 64 and 65.

Table 64

Adsorption Capacity Screening of Steam - Exploded Wood: Seven-Component Solution

Sample	Aniline	Phenol	IsophorOne	Naphthalene	Penta-chlorophenol	Trichloro-ethylene	Bis (2-EtHex) phthalate
Initial Conc'n:							
C_o (1)	4.12	4.08	1.34	1.21	4.79	1.82	3.00
Co (2)	4.37	4.25	1.63	1.45	5.77	2.12	2.33
Adsorbent Load = 50 mg/ 100 ml (Runs 501/ 502);							
C_f (1)	4.10	3.69	0.48	1.07	2.52	1.44	1.80
Cf (2)	3.93	3.84	0.39	1.05	2.50	1.21	2.00
Adsorbent Load = 500 mg/ 100 ml (Runs 5001/ 5002);							
C_f (1)	3.56	3.00	0.51	0.46	BDL	1.38	1.03
Cf (2)	3.44	2.34	0.40	0.64	BDL	1.39	1.20

Notes: Concentrations: Initial, C_o and Final, C_f (in ppm or mg/l)
pH : 3.5 - 4.0
Temp : 20°C
Time: 4 days with agitation
Wood: Steam-exploded Tulip Poplar (-10 mesh)

BDL: Below detectable limits

Table 65

Adsorption Screening of Steam-Exploded Wood: "2, 4-D" and Heavy Metals

Sample	2,4-D	Chromium	Lead
Initial Concentration (ppm)			
C_o (1)	1.64	9.46	9.86
C_o (2)	1.38	10.2	7.83
Adsorbent Load = 50 mg/100 ml (Runs 501/502);			
C_f (1)	1.29	5.69	6.66
C_f (2)	1.30	5.93	6.36
Adsorbent Load = 500 mg/100 ml (Runs 5001/5002);			
C_f (1)	0.75	1.94	4.54
C_f (2)	0.64	1.90	4.66

Notes:
C_f: Final (equilibrium) concentration (ppm)
pH: 3.5 - 4.0
Temp: 20
Time: 4 days (with agitation)
Wood: Steam-exploded Tulip Poplar (-10 mesh)

Table 66

Relative Adsorption Capacities of Steam-Exploded Wood: Model HW Compounds

Adsorbent Dose (M)	Relative Adsorption Capacity (mg/g)			
	Seven-Component Organic Solution	2,4-D	Cr	Pb
0.5 g/l	14.3	0.5	8	4.7
5 g/l	2.8	0.2	1.6	0.9

The resultant adsorption capacities for the seven-component organic solution ("cumulative adsorption capacity") and for chromium, lead, and 2,4-D is given in Table 66.

The results for 2,4-D and for chromium are plotted along with the data obtained for ethanol-extracted lignin and for alkaline-extracted lignin in Figures 56 and 57, respectively.

The results demonstrated rather conclusively that no improvement in adsorption capacity was realized by employing steam-exploded wood as the adsorbent. The magnitude of the adsorption capacities were comparable, for which several explanations were possible:

Assuming the lignin was the "active" adsorbent, no surface-area improvement was evident.

The contribution to adsorption by the cellulosic fiber component was no greater than that of the lignin component and the expected increase in surface area due to the fibrous microstructure was not realized.

Most of the lignin was associated with the -10 mesh sample,filtering through as fine particles and leaving behind a lignin-deficient 10-mesh fibrous fraction.

A surface area measurement was conducted on the screened steam-exploded wood used as adsorbent and its value was found to be a surprisingly low 1.46 m^2/g.

Electron microphotography of the +10 mesh fraction of steam-exploded wood was examined at 100x and 200x (Figure 58) magnifications and compared with the same fraction after having

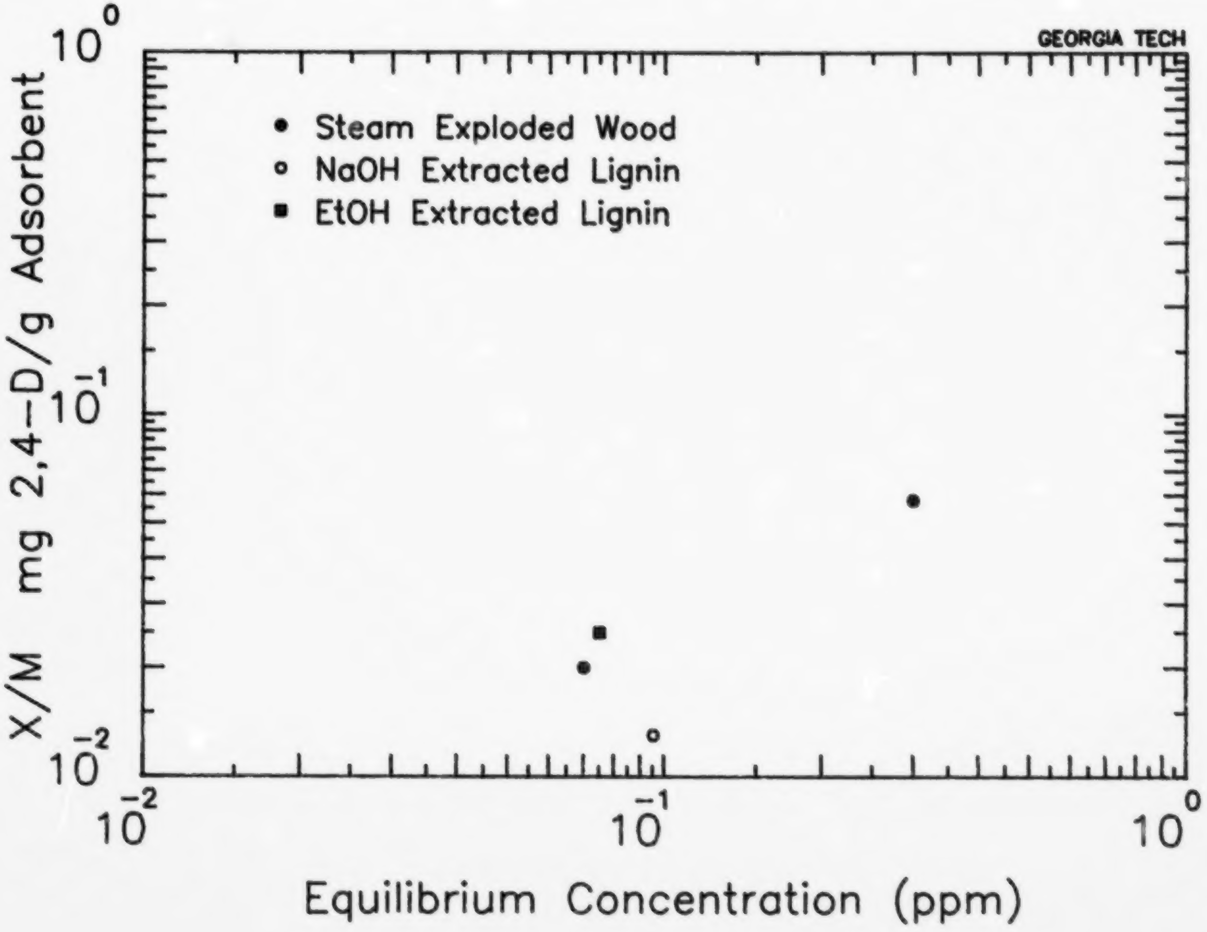


Figure 56 Comparison of Adsorption Capacity of Exploded Wood and Lignin (2,4-D)

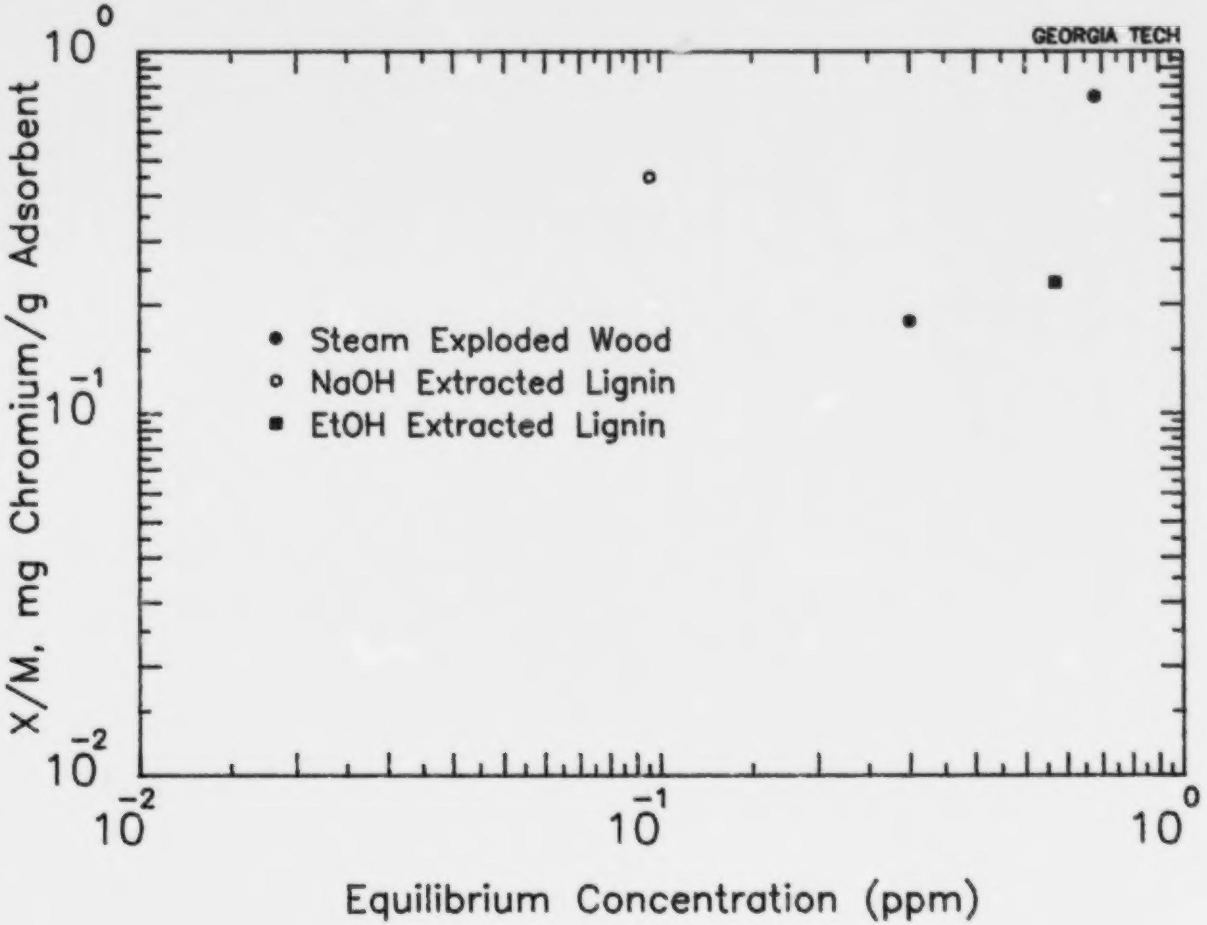


Figure 57 Comparison of Adsorption Capacity of Exploded Wood and Lignin (Chromium).

been delignified by 0.1N sodium hydroxide extraction (Figure 59). The evidence for the existence of discrete lignin particles in steam-exploded wood is striking and is explicable by the occurrence of temperature transitions during hydrothermal treatment whereby the glass transition temperature, softening temperature and melt flow temperature of lignin in the cellular structure of the wood is exceeded, followed by rapid and violent decompression and near instantaneous cooling of the molten lignin with consequent formation of lignin particles, very possibly accompanied by depolymerization and molecular weight reduction. In combination, with the removal of both lignin and hemicellulose (through hydrolytic decomposition), the cellular wall structures of the wood fold, shrink, and collapse with a catastrophic degradation of surface area, porosity and access to the inner surfaces of the cellulose and fibrous structure.

Experiments were initiated to increase the effective surface area of the lignin component by:

(1) re-dissolving the lignin by addition of ethanol to steam-exploded wood and slow rotary evaporation of the ethanol to distribute/deposit the lignin on the fibers,

(2) re-dissolving lignin isolates and coating of high-surface area "inert" supports, e.g. alumina.

Project time and funds expired before the team could demonstrate increases in adsorption capacity with increases in the surface area of the pristine lignin isolates.

Figure 58 Electron Microphotographs of Steam-Exploded wood.

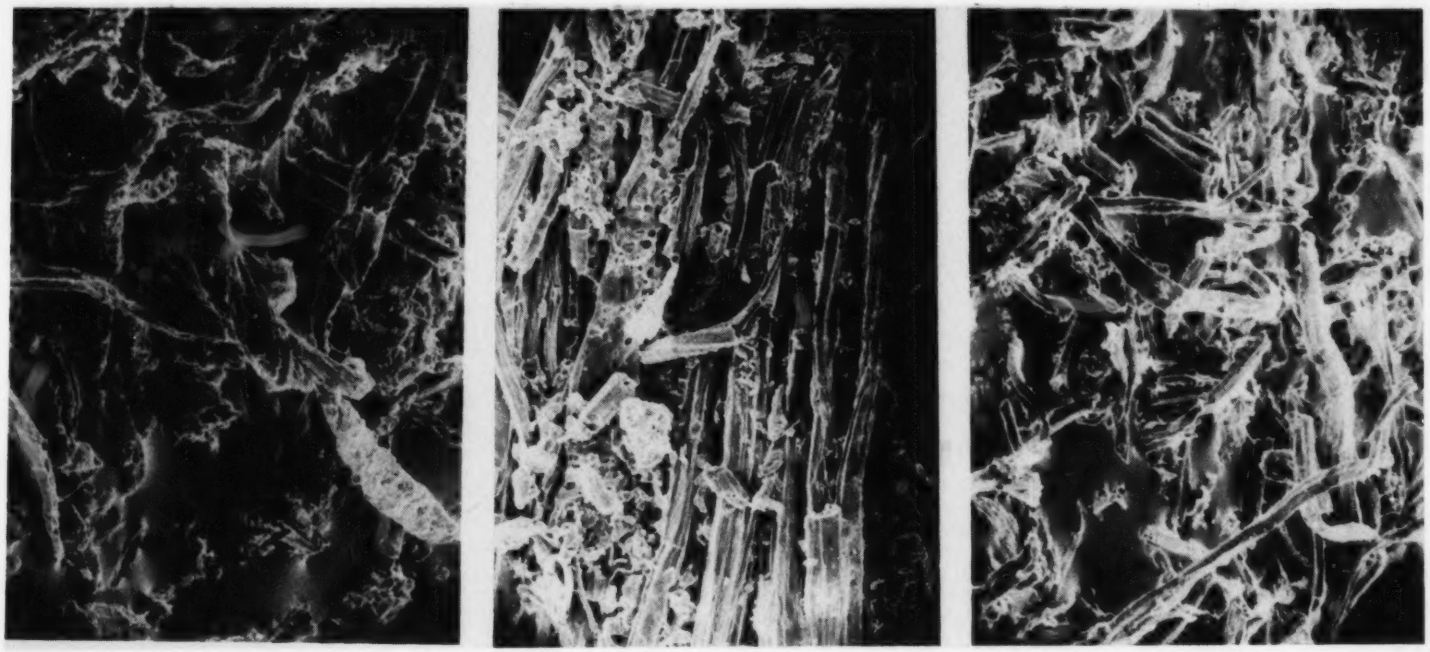


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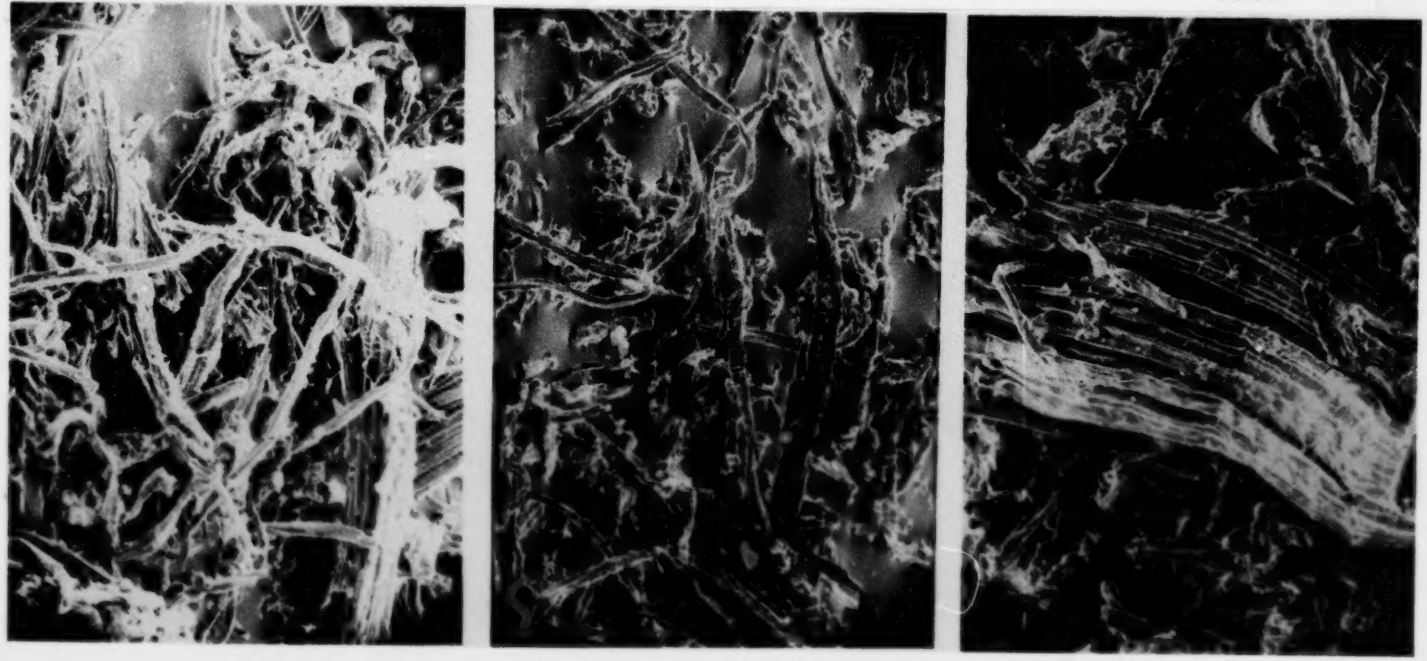
Figure 59 Electron Photomicrographs of Alkaline-Extracted Steam-Exploded Wood.



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